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# Review of the behaviour of colloids in the near field of a cementitious repository Report to NDA RWMD

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### PREFACE

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# Abstract

Colloidal particles (that is particles in the size range 1-1000 nm) have the potential to increase the migration of radioactive species from a geological radioactive disposal facility (GDF) owing to their potential for transporting sorbed radionuclides. Association of radioelements with mobile colloids in the near field potentially may enhance the effective solubility of radionuclides and reduce the effective sorption capacity of the backfill leading to an increase in the radionuclide flux into the host rock. Subsequent migration of radionuclides with groundwater flow through the geosphere may be enhanced by their association with mobile colloids. Consequently, the need to evaluate the potential impact of colloids on the performance of a GDF is recognised in national waste disposal programme world-wide.

This report provides a critical review of the international literature concerning the formation, stability, migration and capacity for radionuclide uptake of colloids in the near field of a cementitious repository, one of the concepts currently under consideration for the disposal of longer-lived wastes in the UK. This review draws principally from three major programmes that have been concerned with cementitious repository concepts for geological disposal; namely those in Japan, Switzerland and the UK. The approaches adopted for the treatment of near-field colloids in performance assessments in these programmes are outlined. The current state of the art of the study of near-field colloids is summarised, and the outstanding questions, priorities and potential approaches to their resolution discussed.

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# **Executive Summary**

Colloidal particles (that is particles in the size range 1-1000 nm) have the potential to increase the migration of radioactive species from a geological radioactive disposal facility owing to their potential for transporting sorbed radionuclides. Colloids that are composed of radionuclide-bearing phases may also be generated in the near field. If radionuclide-bearing colloids are mobile in the near field, the effective solubility of radionuclides may be increased and the effective sorption capacity of the backfill decreased leading to an increase in the radionuclide flux into the host rock surrounding the facility. Subsequent migration of radionuclides with groundwater flow through the geosphere may be enhanced by association of radionuclides 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 potential impact of colloids was the subject of considerable research by Nirex during the 1990s with activities in a range of areas that addressed both generic and site-specific aspects of colloid behaviour. In addition, methodologies for treating colloids in performance assessment (PA) were developed in support of the Nirex 97 assessment of a deep repository at Sellafield, in which the impact of colloids was considered as a potential bias. These calculated radiological risk at very long times arising from <sup>238</sup>U daughters for certain variant scenarios. At that time, the nature, stability and sorption behaviour of near-field colloids were identified as uncertainties that warranted further research to build confidence in their treatment in PA. After 1997, Nirex research on colloids focused on the near field and the characterisation of colloid populations that may arise from leaching the Nirex Reference Vault Backfill (NRVB) and from interactions of cement with wasteform components.

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 the repository concept, a review of the progress made in research into near-field colloids 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 near field of a cementitious repository. The approaches adopted for the treatment of near-field colloids in performance assessments are outlined. The current state of the art of the study of near-field colloids is summarised and the outstanding questions, priorities and potential approaches to their resolution discussed.

In compiling this review, information has been drawn principally from three major programmes worldwide that have been concerned with cementitious repository concepts for geological disposal; namely those in Japan, Switzerland and the UK. Direct intercomparison between the results from these programmes is not always possible. In particular, this is due to differences in specifications for the proposed backfill materials that are designed to condition the near field to high pH. For example, the NRVB has a significantly higher calcium and lower silicon content than the M1 backfill material under consideration in Switzerland. In addition, there have been significant differences in experimental protocols used to study colloid generation from the backfill materials. Nevertheless, a consistent picture appears to be emerging concerning the magnitude of colloid populations under near-field conditions and the controls on their stability.

The main conclusions from this study are as follows.

• Experimental work carried out over the last ten years has found that cementitious colloid populations derived from a variety of potential cementitious backfill materials under simulated near-field conditions are low. Colloid populations are smaller than



those on which the Nirex 97 assessment of a cementitious repository was based. There is a concern, however, about the potential importance of the smaller-sized fraction of the colloid populations, which are not readily accessible to measurement with traditional colloid characterisation techniques. These are expected to have the largest surface area to mass ratio and thus may be significant with regard to available surface sites for radionuclide sorption. In general, the effects of the smallest sized particles (1-3 nm) are taken into account in near-field solubilities which are defined by the use of 30,000 NMWCO filters in solubility experiments. The remaining size gap could be addressed by a systematic filtration study of radionuclide partitioning between different colloidal size fractions in simulated near-field leachates.

- There is a growing body of evidence that colloid populations in environmental systems with low organic concentrations are controlled by the ionic strength of the water, which controls the rate of particle aggregation. The high calcium concentrations in a cementitious near field are expected to destabilise colloids leading to particle aggregation and sedimentation or deposition onto surfaces. As a result, in the absence of significant interaction with organic materials, colloid populations in the near field are expected to be controlled to low levels by the chemical conditions.
- Association of inorganic particles with natural organic compounds is an important mechanism for colloid stabilisation in surface and near-surface waters, where concentrations of natural organic materials may be high. Due to the large amount of organic materials in the UK waste inventory, this mechanism could potentially operate to stabilise and enhance colloid populations in the near-field porewater. Limited experimental evidence to date does not support this contention, however, although this remains an area of uncertainty. Natural, low molecular weight organic materials (fulvic acids), that are alkaline-soluble, may also enter and be stable in the near field; their potential impact on near-field colloid populations (and as complexants of radionuclides) will be a site-specific issue.
- On thermodynamic grounds, cementitious colloids are not expected to be chemically stable but to dissolve on migration from the high pH near field to the low 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.
- There is a lack of published data for sorption of radioelements onto near-field colloids. Only one data point is currently available. Further data would assist in building confidence in the understanding of radionuclide sorption to cementitious near-field colloids.
- Two cases are often considered when treating colloid-facilitated transport of radionuclides in performance assessment: reversible and irreversible sorption of radionuclides onto colloids. At the levels of colloid concentrations measured in experiments and cautious values for sorption distribution coefficients onto colloids, the case of reversible sorption to colloids is not thought to be an issue for repository safety.
- There is uncertainty concerning the reversibility of sorption processes to colloids in general. The treatment of near-field colloids developed for the Nirex 97 assessment, in which the near field is treated as a homogeneous well-mixed system with a uniform distribution of stable and mobile colloids in the transport porosity, requires no assumptions to be made concerning the reversibility of radionuclide uptake to colloids. Thus the approach provides a suitably cautious method for scoping the impact of colloids in the near field on the source term that includes the irreversible sorption case to mobile colloids. Only if such scoping calculations indicate that the impact of the near-field colloid population is potentially significant would consideration of colloids in more complex near-field models be justified.
- In the Nirex 97 assessment, it was found that colloids present in the near field could have an impact on the source term and increase risk from <sup>238</sup>U daughters at long times



should the situation arise that organic complexants are effectively removed from the near field. However, if recently measured colloid populations levels are combined with the cautious sorption distribution coefficients for near-field colloids and in the absence of significant concentrations of organic materials, then there would be no significant colloid-associated radionuclide load in the near field. Given the uncertainties noted above, this conclusion should be treated cautiously for the time being; additional experimental data addressing these specific uncertainties would build confidence in this conclusion.

- If sorption to colloids is found to show significant irreversibility and colloid particles are found to persist then there may be a need to develop further understanding of colloid mobility and chemical stability in the near field and into the far field. However, the same processes by which radionuclides may be irreversibly sorbed to colloids are also likely to occur at the surfaces of cements and rock. In reality, given that near-field colloids are expected to have limited persistence (i.e. finite lifetimes) in the geosphere, the effects of radionuclide retardation by immobilisation with solid phases are likely to outweigh the detrimental effects of transport of radionuclide irreversibly bound to near-field colloids.
- The association of particles (including larger particulates) with the surfaces of gas bubbles (flotation) or droplets of LNAPLs may provide mechanisms for particle transport out of the near field by buoyancy-driven flow. Owing to uncertainties concerning the impact of gas transport and the formation and transport of NAPLs in a repository, assessment of the significance of flotation and LNAPLs-associated particle transport does not yet seem appropriate.



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# **Abbreviations**

ACW	Artificial cement water (term used on Swiss programme)
ADZ	Alkaline disturbed zone
AEAT	AEA Technology
AF4	Asymmetric flow field flow fractionation
AFM	Atomic force microscopy
BFS	Blast furnace slag
BGS	British Geological Survey
BSE-SEM	Backscattering electron-scanning electron microscopy
BVG	Borrowdale Volcanics Group
CASH	Calcium aluminium silicate hydrate
CCC	Critical coagulation concentration
CEW	Cement-equilibrated water
CFM	Colloid Formation and Migration (experiment in Grimsel URL)
COLEX	Column experiments (principally two-phase flow in cement run by PSI)
CoRWM	Committee on Radioactive Waste Management
CRIEPI	Central Research Institute of the (Japanese) Electrical Power Industry
CRR	Colloid and Radionuclide Retardation (experiment in Grimsel URL)
CSH	Calcium silicate hydrate
DLVO	Derjaguin, Landau, Verwey and Overbeek
DOC	Dissolved organic carbon
EBS	Engineered barrier system
EC	European Commission
EDX (EDAX)	Energy dispersive X-ray analysis
ELT	Equilibrium leach test
EXAFS (XAFS)	) Extended X-ray absorption fine structure (spectroscopy)
FEP	Feature, event or process
FFFF	Flow field flow fractionation



GDF	Geological disposal facility
GPA	Generic Performance Assessment
GTS	Grimsel Test Site
HLW	High-level (radioactive) waste
HFSC	High flyash and silica fume-content cement
HPF	Hyperalkaline Plume in Fracture Rock (experiment in Grimsel URL)
ILW	Intermediate-level (radioactive) waste
ISA	Isosaccharinic acid
JAEA	Japanese Atomic Energy Agency
LIBD	Laser-induced breakdown detection
LLW	Low-level (radioactive) waste
LLWR	Low-level (radioactive) Waste Repository facility located at Drigg, Cumbria, UK
LNAPL	Light non-aqueous phase liquid
LSC	Long-term Cement Studies (experiment at Grimsel URL)
M1	Candidate mortar backfill composition developed on the Swiss Programme
MRWS	Managing Radioactive Waste Safely
Nagra	Swiss radioactive waste disposal agency
NAPL	Non-aqueous phase liquid
NDA	Nuclear Decommissioning Authority
NEA	Nuclear Energy Agency
NMWCO	Nominal molecular weight cut-off (filter specification)
NRVB	Nirex Reference Vault Backfill
OPC	Ordinary Portland cement
PA	Performance assessment
PCM	Plutonium-contaminated material
PCS	Photon correlation spectroscopy
PFA	Pulverised fuel ash
PGRC	Phased Geological Repository Concept

POC	Project Opalinus Clay
PSI	Paul Scherrer Institute, Switzerland
PZC	Point of zero charge
PZHS	High sulphate-resistance Portland cement (investigated on Swiss programme)
REE	Rare earth element
RWMD	Radioactive Waste Management Directorate (of NDA)
SEM	Scanning electron microscopy
SF	Spent (nuclear) fuel
SKB	Swedish Nuclear Fuel and Waste Management Company
SLST	Solubility-limited source term (near-field model)
S/L	Solid to liquid ratio
SPC	Single particle counting
SPLITT	Split-clow thin-cell fractionation
ТЕМ	Transmission electron microscopy
TRU	Trans-uranic (wastes)
UKAEA	United Kingdom Atomic Energy Authority
UK DoE	United Kingdom Department of the Environment
URL	Underground research laboratory
USD	Uranium-series disequilibrium
VLLW	Very low-level (radioactive) waste



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## 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]. This followed the publication of the recommendations of the independent Committee on Radioactive Waste Management (CoRWM) in July 2006 [2]. The Nuclear Decommissioning Authority (NDA) is the body charged by Government with planning and implementing geological disposal in the UK. This responsibility is being discharged by its Radioactive Waste Management Directorate (NDA RWMD) which was set up to develop an effective delivery organisation to implement a safe, sustainable and publicly acceptable geological disposal programme. This mission builds on the work of United Kingdom Nirex Limited (Nirex), which was subsumed into the NDA in November 2006.

Geological disposal facilities for the long-term isolation of both intermediate-level (ILW) and certain long-lived low-level (LLW) radioactive wastes are in various stages of development in a number of countries (see reference [3] for an overview), including the UK [4,5]. Such facilities utilise a combination of engineered and natural barriers to form a multi-barrier containment system, the concept is illustrated in Figure 1.1. Physical containment of radioelements would be achieved by immobilisation and packaging of wastes (mostly) in stainless steel containers. Geological isolation would be achieved by emplacement of the waste packages in vaults excavated deep underground within a suitable geological environment. 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 the repository's lifetime [6].

This report focuses on colloids associated with a generic cementitious repository for ILW and certain LLW because there is some evidence that these may be generated in the near field of a deep repository [e.g. 7,8,9,10]. If radionuclides are associated with these colloids and the colloids are mobile, the effective solubility of radionuclides may be increased and the effective sorption capacity of the backfill decreased. This may lead to an increase in the flux of radionuclides from the repository into the surrounding host rock [11]. Subsequent migration of radionuclides with groundwater flow through the geosphere may be enhanced by association of radionuclides 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 [e.g. 12, 13, 14, 15]. For example, HSK, the Swiss Nuclear Safety Inspectorate, stated [16] that "...possible colloid associated transport of radionuclides remains an important open question." This was more recently echoed in JAEA's Second Progress Report on TRU Waste [17], where it was noted that "It is suggested that the concentration of these (cement) colloids will be low and their influence on nuclide sorption will be small." but, nevertheless, the report went on to note that colloids would not be excluded from consideration because "There is a significant quantity of colloids in the cement pore water. Furthermore, because colloids are produced by disturbances to the groundwater, in this situation (for example, influences of excavation, etc.), the production of colloids caused by repository construction (also) cannot be ruled out".

Consequently, many national programmes have undertaken research into colloids [e.g. 13,16,18]; this includes work undertaken by Nirex in the UK [e.g. 19,,20,21,22,23]. This



research has covered a range of colloid types (e.g. cement, metal, natural, organics, etc) and formation/migration processes, including transport by gas bubbles [e.g. 24].



# Figure 1.1 Schematic representation of the geological disposal concept for ILW and long-lived LLW [5]

In the UK, work on the potential impact of colloids on radioactive waste disposal was initiated at the Harwell laboratories of the UKAEA in the mid-1980s and pioneering studies of colloid generation and interactions in a cementitious repository [25] and colloid-facilitated transport in the geosphere [26] were undertaken with funding from UKDoE and the EC. On the Nirex programme, the potential impact of colloids was the subject of considerable research during the 1990s with activities in a range of areas that addressed both generic and site-specific aspects of colloid behaviour. The Nirex work was concentrated into 6 main areas.

- Colloid generation from near-field cementitious materials (in particular NRVB) [19,27,28,29].
- Colloid analysis of leachates from equilibrium leach tests (ELTs) [30,31].
- Site-specific colloid sampling and characterisation studies including the measurement of colloid populations and distributions of natural uranium series isotopes in groundwaters [e.g. 22,32,33]. This work was undertaken when the Longlands Farm site near Sellafield was being investigated as a possible location for a repository for ILW and certain LLW.
- Laboratory-based studies of colloid stability and surface properties using synthetic and site-specific colloidal materials [21].
- Colloid transport experiments through fractured geological materials including both laboratory-based and field experiments [21,34].

• Interpretive modelling of laboratory migration data using simple models of colloid transport and retardation [21].

In addition, methodologies for treating colloids in performance assessment (PA) were developed [35] in support of the Nirex 97 assessment of a deep repository at Sellafield, in which the potential impact of colloids was considered as a potential bias [36]. These calculations found that the presence of near-field colloids could potentially increase the calculated radiological risk at very long times arising from the <sup>238</sup>U daughters for certain variant scenarios (see also discussion in Section 6). At that time, the following uncertainties were identified concerning the behaviour of colloids that warranted further research to build confidence in the treatment of colloids in PA [35]:

- the nature, stability and sorption behaviour of near-field colloids;
- the nature, stability and mobility of colloid populations in the alkaline disturbed zone (ADZ<sup>1</sup>);
- the extent to which sorption of radionuclides to colloids is irreversible.

After 1997, Nirex research on colloids focused on the near field and was concerned primarily with characterising colloid populations produced on leaching the NRVB, initially through leaching of granulated material and later through studies of monolith leaching [19,28,29]. Colloid studies were also undertaken on leachates from two ELTs that were designed to simulate the situation in a repository after closure and which were run for nearly seven years [30,31]. The ELTs contained a mixture of real intermediate level wastes with the principal near-field components (waste, encapsulation matrix, container and backfill). Through these studies, significant progress was made in identifying the main types of colloids produced from the NRVB, the nature of colloid types generated from wasteform components and in the measurements of colloid populations and size distributions (within the limitations of the experimental techniques).

Since the early 1990s, work on colloid generation from potential cementitious backfill materials has also been undertaken on the Japanese and Swiss programmes and attempts have been made to isolate and measure colloid populations in the alkaline cement-like waters at the Maqarin natural analogue site in Jordan. Work is currently in progress to assess colloid populations at the Mangatarem site in the Philippines, an analogue for a low-alkali cement environment. Experimental and modelling studies of the stability of near-field colloids have also been undertaken on the Swiss and Japanese programmes and some limited studies of radionuclide sorption onto cement-derived colloids (although little information has as yet been published).

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 the repository concept, a critical review of the progress made in research into near-field 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 near field of a cementitious repository. The current state of the art of the study of near-field colloids is

<sup>&</sup>lt;sup>1</sup> In the UK programme, the near-field chemical conditions, where the pH is buffered for a very long time by calcium hydroxide to values of about 12.5, have been referred to as alkaline. In general, the term alkaline refers to solution pH values greater than neutral. Elsewhere the term hyperalkaline (i.e. excessively alkaline) has been used to describe cementitious near-field chemical conditions. However, there is no clear consensus in the literature concerning the distinction between alkaline and hyperalkaline conditions.



summarised and the outstanding questions, priorities and potential approaches to their resolution discussed.

In compiling this review, information has been drawn principally from three major programmes worldwide that have been concerned with cementitious repository concepts for geological disposal; namely those in Japan, Switzerland and the UK. Much of the work on near-field colloids has been presented in peer-reviewed journals in the open scientific literature as well as in contractor's reports. Contractor's reports to Nirex have undergone an independent expert review prior to publication.

One point that needs to be made at the outset, is that direct intercomparison between the results from these programmes is not always possible. In particular, this is due to differences in specifications for the proposed backfill materials that are designed to condition the near field to high pH. For example, the NRVB has a significantly higher calcium and lower silicon content than the M1 backfill material under consideration in Switzerland [37] and the use of low pH and high silicon content cements is under consideration in the Japanese programme [e.g. 38]. In addition, differences in the nature of the waste streams, wasteform specifications (e.g. use of different types of encapsulation materials) and other aspects of the repository design will have a bearing on the evolution of near-field chemistry that may impact on potential colloid populations and stability in the near field. For example, as shown in Table 1.1, there are significant differences in the simulated cement porewaters used around the world for radioelement sorption and solubility experiments.

Parameters	UK	Switzerland	Japan	Finland
Porewater type	NRVB- equilibrated deionised water	VB- brated ed water brated brated brated brated brated brated brated brated brated brated brated brated brated brater brated brated brater bra		Cement leachate ALL-MR f63, low alkali grout porewater
pН	12.5	12.5 13.3 13.18		10.05
Na	1.9 × 10 <sup>-4</sup>	0.114	0.104	0.191
К	$6.4 \times 10^{-4}$	0.182	0.100	$3.85  imes 10^{-3}$
Са	1.5 × 10⁻²	1.6 × 10 <sup>-3</sup>	$2.4 \times 10^{-3}$	1.1 × 10 <sup>-3</sup>
Si	$3.9  imes 10^{-5}$	$4 \times 10^{-5}$	2.11 × 10 <sup>-3</sup>	5.35 × 10⁻⁵ (as SiO₂)
AI	7 × 10 <sup>-6</sup>	5 × 10 <sup>-5</sup>	$7.02  imes 10^{-5}$	No data
S $2 \times 10^{-5}$ $3 \times 10^{-3}$ $2.1$		$2.16\times10^{-4}$	$2.57  imes 10^{-3}$ (as $SO_4^{-2}$ )	
CO3 <sup>2-</sup>	≤7 × 10 <sup>-4</sup>	1.2 × 10 <sup>-4</sup>	No data	No data
Reference	39	40, 41	17	42

## Table 1.1 Comparison of the experimental cement porewaters used for cement sorption and colloid studies on different programmes (units mol dm<sup>-3</sup>)

Finally, it is also noted that the use of cement additives, in particular superplasticisers, is under consideration in a number of programmes (e.g. Japan, Finland). These materials, which may be colloidal in their own right, would be used to reduce the water demand and improve rheological properties of cements. These changes in cement properties arise from the



stabilising effect of the admixtures on cement particle dispersions [e.g. 43], which potentially may have implications for cement colloid generation. As far as these authors are aware, no firm decisions have yet been made in any of the above programmes concerning the use of such materials or which precise formulations might be used. Therefore, it is too early for significant investment to have been made into their potential impact on near-field colloid populations.

### **1.2** Approach to addressing the colloid issue and the scope of this review

As noted above, the question of the potential importance of colloids to the performance of a cement-based geological disposal facility remains something of an open issue. To address the issue, a structured approach is required. It is generally recognised that to account for the possible effect of colloid-facilitated transport in a performance assessment it is necessary to address a number of key questions concerning the likely colloid behaviour for the chosen repository concept at the particular site under consideration. Figure 1.2 shows an example of a simple conceptual scheme or decision tree as a basis for assessing the potential importance of colloids in the near field. The decision tree consists of a series of yes/no questions concerning may be recommended for the treatment of colloids in an assessment (which are not specified in detail in Figure 1.2). Similar conceptual schemes can be constructed for the treatment of colloids in the far field (e.g. Figure 1.1 in [20]).

The decision tree provides a framework for both designing a focused R&D programme into the role of colloids and for assessing its progress. Since the early 1990s, near-field colloid studies on the Nirex programme, and a number of other programmes internationally concerned with cementitious repositories, have focused on the potential for generation, stability and mobility of colloids in the repository near field. Owing to the relatively low colloid concentrations measured to date in most of these studies, rather less emphasis has been placed on studying the association of radionuclides with near-field colloids and their migration behaviour. Nevertheless this review will consider the progress in addressing each of these key questions in the UK and internationally.

It is important to note that work on colloids both in the near and far fields has built on existing understanding of colloid behaviour, developed over many years in the field of colloid science. In this report, emphasis will be placed on processes affecting inorganic particles, which have been the primary concern in cementitious repository systems owing to the high sorption capacity of minerals that may potential form near-field colloids (such as calcium silicate hydrate (CSH) gels, which are major components of cementitious materials, and iron oxide minerals that will arise as steel corrosion products). The potential role of organic waste materials and their degradation products that may act as complexants for radioelements and their treatment in performance assessment have been dealt with separately on the UK and other programmes.

The main issues relating to the role of near-field colloids are discussed in sub-section 1.5 and the scope of the near-field colloids research undertaken worldwide outlined. The work undertaken to address the key questions concerning the presence, stability, radionuclide sorption and migration behaviour of near-field colloids are reviewed in Sections 2, 3, 4 and 5, respectively. In each Section, the current understanding of these aspects of colloid behaviour is summarised.

The omission of colloids was identified as a potential bias in the Nirex 97 post-closure performance assessment of a deep repository at Sellafield [36]. Based on the current understanding at that time, equations were developed to include colloid-facilitated radionuclide transport into the Nirex 97 assessment models and a number of deterministic scoping calculations were performed to investigate the bias due to the omission of colloids both in the near and far fields [35]. Two of these calculations were reported with Nirex 97. Although over 10 years old, Nirex 97 and supporting studies remain the most recently published assessment calculations in which the potential role of near-field colloids was treated in detail. The



# Figure 1.2 Example of a colloid decision tree for the near field of a radioactive waste repository



mathematical treatment adopted for colloids in the near field is outlined and the results of scoping calculations are reviewed in Section 6. The approaches adopted to the treatment of near-field colloids in a number of other assessments of cementitious repositories undertaken internationally are discussed for comparison. Finally, the current state of understanding of the key questions for colloids in the near field are summarised in Section 7 and the outstanding questions, priorities and potential approaches to their resolution discussed.

## 1.3 Definition of colloids

In 1861, the Scottish chemist Thomas Graham coined the term *colloid* (from the Greek for "glue") to describe certain solutions, known as Selmi's "pseudosolutions" [44], 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 [45].

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 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. 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<sup>2</sup>" [46]. 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  $0.45 \,\mu$ m) as this is the 'standard' filter pore size used when sampling ground-, pore- and seawaters [e.g. 47, 48, 49, 50]. In colloid studies, this standard pre-filter may then be followed by sequential filtration through a range of filters with increasingly smaller pore sizes [cf. 12, 13].

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 of actinide elements were widely referred to as 'real colloids' and 'pseudo-colloids' (after [7]), respectively, but this practice is becoming less common.

<sup>&</sup>lt;sup>2</sup> This terminology is designed to include systems such as slurries of long needle-like particles and thin liquid films which are colloidal in one and two dimensions, respectively.

## **1.4** Types and sources of colloids in the near field and the far field

In considering the potential role of colloids in the transport of radioactivity from a deep cementitious repository into the surrounding host rock, two sources of colloids and their behaviour under near-field conditions need to be considered:

- the colloid population in the groundwater which may be transported into the repository by groundwater flow; and
- colloids that may be generated in the repository, *in situ*, from the degradation of near-field materials, i.e. near-field colloids.

Colloid characterisation programmes for a wide range of groundwater systems, world-wide, have shown that colloids are present in all groundwaters, at mass concentrations ranging from  $0.1 \,\mu\text{g} \,\text{dm}^{-3}$  to 100 mg dm<sup>-3</sup> [e.g. 51, 52, 53, 54]. The highest colloid mass concentrations have been measured in organic- (humic-) rich groundwaters, such as those at the Gorleben site in Germany [52]. However, in deep systems (over 300 m depth), with low organic contents, colloid populations, comprising predominantly inorganic mineral particles, have mass concentrations typically less than 1 mg dm<sup>-3</sup> [55]. 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/aquifer system. Such colloids may contribute to radionuclide transport within the near field if they are stable within the near-field environment.

The nature of colloids generated within a repository, is a more generic issue relating to the nature of the wastes and the choice of materials selected to provide the engineered barriers such as waste encapsulation grouts, waste containers and the cementitious backfill material, although near-field colloid populations may also be dependent on the chemistry (e.g. salinity) of the groundwater.

Although this review is concerned primarily with the formation and behaviour of near-field colloids, the general behaviour of typical far-field colloidal materials under near-field conditions will also be discussed.

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 a continuum exists between inorganic colloids (clay, oxides), inorganic colloids coated with organic material, organic colloids associated with inorganic phases and organic colloids [54]). 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. 56].

Inorganic colloids in groundwater are generated primarily by the physical disintegration and weathering of rock in contact with water [57] (also termed primary colloid generation [55]). Colloids may also be formed under conditions where the groundwater chemistry is not in equilibrium with the primary mineral composition [e.g. 19, 58, 59] (e.g. supersaturation is reached with respect to secondary minerals at a redox front). As chemical equilibrium is re-established, changes in both groundwater chemistry and mineral phases will occur that can lead to the precipitation of new crystalline or amorphous phases; colloids may be produced by homogeneous nucleation and growth processes. These processes have been termed secondary colloid generation [55]. However, there will be competition between rock surface sites, nucleating colloids and existing colloids for secondary phase growth [60]. Modelling suggests that precipitating solids may attach predominantly to the rock surfaces if the relative colloid surface area is low [60].

Generally, assuming the deep groundwater is in equilibrium (i.e. with no redox, salinity or pH fronts in the vicinity), the inorganic colloids can be assumed to reflect the nature of the host rock and be comprised of mineral fragments of the rock matrix (e.g. quartz, feldspar, clays) or



secondary minerals from the groundwater flowpaths, (e.g. clays, iron oxide, calcite). For example, in Nagra's Grimsel URL, where the natural groundwater colloids have been studied extensively [e.g. 55,61,62], the host rock is a granodiorite with a dominant mineralogy of quartz, feldspar and biotite and a wide range of minor phases (see column 2, Table 1.2). The groundwater advects through fractures where the fracture mineralogy is slightly modified from this (columns 3 and 4, Table 1.2) and the colloids consist of quartz, biotite, muscovite, illite and Ca-silicates (plagioclase feldspar) [62], closely echoing the predominant phases in the fractures and host rock.

Mineral	Weakly foliated granodiorite (vol %)	Mylonite (vol %)	Fault gouge (vol %)
Quartz	23	17	15
Plagioclase	23	32	28
K-feldspar	20	11	7
Biotite (with illite inclusions)	14	30	41
Chlorite	3	<1	<1
Muscovite	8	5	4
Epidote	5	3	3
Sphene	2	2	2
Rutile	trace	trace	trace
Zircon	trace	trace	trace
Sphene	2	2	2
Rutile	trace	trace	trace
Zircon	trace	trace	trace
Apatite	trace	0.25	trace
Calcite	-	trace	trace

## Table 1.2Average mineralogical compositions of different portions in and behind the<br/>MI shear zone (AU 96) in the Nagra URL at Grimsel (after [63]).

Indeed, to date, only one case is known [62] where the groundwater colloids did not represent the host rock in the area sampled, but that of a neighbouring granite, some 5 km from the sampling point, indicating potential long-distance transport of colloids in a deep groundwater. However, as groundwater was extracted at high flow through relatively wide fractures (1-10 cm) and the local ionic strength was rather low, promoting colloid stability, conditions were rather far from those expected in a deep groundwater<sup>3</sup>.

In the vicinity of a redox front, colloidal iron oxyhydroxides are to be expected, perhaps along with colloidal sulphur species and, rarely, manganese oxide colloids [e.g. 58]. In such systems, 'normal' rules for colloid stability can be changed, at least locally (see Section 3).

<sup>&</sup>lt;sup>3</sup> Degueldre has commented [55] "...the results should not be over-interpreted".



Hydrodynamically-induced release (i.e. erosion) of colloids has also been studied, principally in soil science. Experimental and modelling studies of colloid production by erosion have provided a basic understanding of the processes involved - for example, that the rate and extent of colloid detachment increases as the flow velocity and particle size increase [64] and that a critical shear stress must be attained to initiate erosion [65]. Nevertheless, it was recently noted 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." [66]. In the opinion of these reviewers, it may be argued that such erosive production of colloids is of little relevance to a geological repository (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 repository), but the process has to be kept in mind when examining existing data for near-field colloids due to some of the experimental methods employed (see sub-section 2.5.2 for further details). Interestingly, potential erosion of bentonite colloids from the repository backfill and buffer 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 [16,67] for details) and the Colloid Project in the Aspö URL in Sweden [68].

Although organic macromolecular colloids are present in groundwaters in true solution, they are 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 [69]. Organic macromolecules may act as carriers 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 and their sorption capacity for radionuclides.

Colloids may be generated in the near field of a repository by similar mechanisms to those occurring in groundwater systems. In a cementitious repository, the near field composition and chemistry will be dominated by the cementitious backfill and wasteform grout materials. This is illustrated in Figure 1.3 which shows the relative compositions of materials envisaged in current designs for ILW and LLW repositories in Switzerland.

Colloids may be generated by the physical disintegration (spalling) of the cement matrices in contact with water [e.g. 19] and the corrosion of metallic constituents of the wastes (e.g. steels, Magnox, zircaloy, aluminium), waste containers and other metal structures within the repository [e.g. 70]. Ramsay [8], recognising that cement is essentially a colloid-based material, highlighted the potential formation of colloids from the cementitious backfill and waste encapsulation grouts by the dissolution and reprecipitation of cement phases. Colloids may also grow by aggregation processes 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 collision (see Section 3 below).

Intrinsic radionuclide colloids (or radiocolloids) may be formed in the near field [e.g. 71] and they may be advected into the surrounding rock with the groundwater [13]. Intrinsic colloids may be generated by similar mechanisms as carrier colloids, where the waste mineral phases concerned contain a significant radioelement component.

Colloids may also be generated in the alkaline disturbed zone of the geosphere where the host rock is contacted by the alkaline plume eluted from the repository [72].

Organic colloids can be produced from the degradation of organic materials in the waste such as cellulosic materials (e.g. wood, paper) and polymeric materials [e.g. 73,74] or from plasticisers in the grout or backfill [e.g. 75]. In addition, it is possible that as-disposed organic materials or their degradation products may interact with inorganic colloids generated in the near-field in a similar way that natural organic materials interact with inorganic colloids in the geosphere.





## Inventory of an ILW repository

Figure 1.3 Relative proportions of material present in a LLW and an ILW repository: example of the Swiss inventory. Image courtesy of Nagra

## 1.5 Key Questions Concerning the Role of Colloids in Radionuclide Transport

In general, work undertaken to address the potential role of near-field colloids has followed a structured approach designed to answer a number of key questions concerning the likely behaviour of colloids and their impact on radionuclide transport; see the framework shown in Figure 1.2. Below is a brief commentary on each of the questions in Figure 1.2 and the related activities that have been undertaken both in the UK and worldwide to address them. In particular, where there is relatively little knowledge available directly, potential sources of related information which can be used to inform discussion of the likely behaviour of near-field colloids are indicated. The commentary below indicates also where the material outlined is discussed in more detail in this report.

## Qu. 1. Are there potentially significant numbers of groundwater colloids that are stable in the near field?

This is partly a site-specific question and partly a generic one. Clearly, the nature of the groundwater colloid population that may be transported into the repository near field is a site specific issue. However, the question of its stability under near-field conditions can be treated more generically. As noted previously, colloids are known to be present in all groundwaters, at concentrations ranging from 0.1  $\mu$ g dm<sup>-3</sup> to 100 mg dm<sup>-3</sup>. A brief overview of the understanding of colloid populations in groundwaters will be given in Section 2, partly to put measured near-field populations (see Qu. 2.) into a wider context.

If groundwater colloids are stable and mobile in the alkaline environment of the near field, they may potentially play a role in facilitating the transport of radionuclides from a repository. The stability behaviour of many types of colloidal systems has been studied in the laboratory including the stability of model groundwater colloids in cementitious waters, which generally have indicated limited stability under near-field conditions [e.g. 26]. Generic studies of colloid stability behaviour under near-field conditions are reviewed in Section 3.

#### Qu. 2. Are there potentially significant numbers of stable near-field colloids?

This question is really in two parts, colloid presence and colloid stability, although in many respects these two parts are closely related, because stability may be the determining factor controlling colloid populations measured in experiments.

The potential for the generation of colloids from near-field materials, in particular cementitious grout and backfill matrices, has been investigated on a number of waste management programmes including the UK, Switzerland and Japan. In addition, attempts have been made to isolate and measure colloid populations in the alkaline cement-like waters at the Maqarin natural analogue site in Jordan. In general, the results of such studies to date have indicated that colloid concentrations in near-field waters are rather low. Studies of colloid populations are described in Section 2 of this report.

For colloids to play a role in facilitating the transport of radionuclides from the near field, they must be stable under near-field conditions. Studies of the stability of near-field colloids have also been made on the above programmes; the results of these studies are reviewed in Section 3.

## Qu. 3. Are there potentially significant concentrations of radionuclide-bearing colloids in the near field?

Near-field colloids will only play a significant role in radionuclide transport if there is a significant loading of entrained colloids with radionuclides. This will depend on the strength of sorption of the various radionuclides onto surfaces. Colloid-facilitated transport is anticipated to be more significant for more strongly sorbing radionuclides, the solubility of which may also be low. Limited studies of radionuclide sorption onto near-field colloids have been made on the Nirex programme [19]. However, owing to the rather low concentrations of near-field colloids that have been measured in colloid generation studies to date (Qu. 2.), relatively little work has been undertaken to study sorption onto near-field colloids internationally.

Rather more information on sorption to model colloids (usually synthetic) under a range of conditions is available in the general scientific literature and the study of uranium and thorium series isotope distributions in solution and associated with natural colloids, which often has been carried out alongside groundwater colloid characterisation



studies, provides useful background for understanding the likely sorbent behaviour of near-field colloids. Radionuclide association with near-field colloids is discussed in Section 4.

#### Qu. 4. Are colloids mobile in the near field?

At a conceptual level, it should be self-evident that unless colloids are mobile through the near field they cannot contribute to radionuclide transport, although they may contribute to radionuclide retardation. Colloid mobility may be influenced by the geometry of the flowing features in the repository such as fractures and the permeability and pore-size distributions of cement matrices.

However, at the practical level, this question represents a level of detail that has yet to be addressed in most performance assessments of cementitious repositories because many have used source term models that treat the near field as homogeneous and uniform (e.g. Nirex 97 [36]). Thus, mobility of all radionuclides and colloids (if treated), to the near-field/far-field interface is assumed. Thus, the cautious assumption has been made that colloids are mobile in the near field.

This question only needs to be addressed if more complex radionuclide release models are required that include treatment of transport processes in the near field in some way and if there is evidence that the answers to Qus. 2. and 3. are yes.

For the above reasons, the mobility of near-field colloids, *per se*, within the repository near field has not been investigated. Some general comments concerning colloid mobility in the near field will be made in Section 5, which is concerned principally with a discussion of migration of colloids from the near field into the geosphere.

#### Qu. 5. Are colloids excluded from the non-flowing porosity?

This is a minor question concerning near-field colloid behaviour, but is retained in the decision tree because it may be necessary to consider colloid exclusion in the source term model in assessments depending on the conceptual model for transport in the near field.

Although homogeneous source term models such as that in Nirex 97 do not include migration in the near field, exclusion processes are accounted for in such models because within the underlying conceptual model it is recognised that exclusion may reduce the capacity of the repository to retard the release of radionuclides. It is well-established that radionuclides in anionic or complexed forms and colloids may be excluded from some of the finer-scale porosity in grout and backfill materials. Owing to their size as well as charge, colloids may be excluded from significant proportions of the non-flowing matrix porosity that are accessible to dissolved radionuclides.

Both the volume of pore water into which radionuclides may dissolve and the area of matrix pore surfaces of the backfill onto which radionuclides may sorb may be reduced due to exclusion processes. This may lead to an increase in concentrations of certain radionuclides leaving the repository, which may be increased further by association of radioelements with mobile colloids that are excluded from significant portions of the matrix pore volume.

The ability of colloids to diffuse into the non-flowing porosity of hard rocks has been investigated in a number of studies [e.g. 76], but not to the authors' knowledge in cementitious materials. Colloid exclusion will be discussed specifically in the context of the near-field/far-field interface in Section 5 (see Qu. 7. below).



#### Qu. 6. Are radionuclide-colloid associations reversible?

If radionuclides become irreversibly incorporated into colloids or desorption is a slow process compared to groundwater residence times in the near field, then transport of radionuclides may be accelerated relative to the case where sorption onto colloids is a reversible process. The rate of colloid-bound radionuclide transport is then determined by the transport behaviour of the colloids. In the case where colloids are mobile and unretarded, and radionuclide attachment to the colloid is irreversible, there is the greatest potential for colloids to impact on radiological risk.

This is perhaps the most difficult question concerning the role of colloids to address experimentally. Few specific studies of sorption to near-field colloids have been reported and there is little information available on the reversibility of sorption to near-field colloids *per se*. However, the question of sorption reversibility is a topic of general interest in the sorption field and studies have been reported of desorption kinetics from materials such as host rocks [e.g. 77] and bentonite [e.g. 78], but not cementitious materials. In addition, this question has received considerably attention in far-field colloid studies from the application of uranium series disequilibrium studies (USD) to investigate whether uranium or thorium bound to colloid particles is in thermodynamic equilibrium with dissolved species. (Although, natural uranium and thorium concentrations measured in groundwaters are frequently insufficient for conclusions to be drawn concerning the nature of the actinide-colloid interactions.) Therefore information on the likely reversibility of sorption to near-field colloids can be sought from general studies of sorption reversibility and far-field colloid studies. This subject is discussed in Section 4.

#### Qu. 7. Do near-field colloids enter the geosphere?

This question addresses whether colloids that may be formed in the near field are able to migrate by diffusion or advection into the geosphere. If near-field colloids are stable in the chemical conditions in the geosphere they may potentially be mobile and act as radionuclide carriers and therefore need to be considered in the far-field transport model.

Colloid migration into the geosphere may be prevented due to chemical, physical or physico-chemical means. In the context of a cementitious disposal facility, the near field will become surrounded by an alkaline-disturbed zone as a result of interactions between the plume of alkaline water and the host rock. There will be significant gradient in chemical properties (pH, main element concentrations) between the proximal and distal regions of the plume. This chemical gradient may have a significant effect on the nature, stability and mobility of colloids.

This question will be discussed based on current understanding of the evolution of alkaline plumes and likely colloid behaviour in Section 5.

In a number of cementitious repository concepts under consideration internationally, the near field may be surrounded by a clay buffer [e.g. 17] or be located in a clay formation [79,244] that may be impermeable to the migration of colloidal species. In the absence of fractures or other dislocations in the surrounding clay, it is likely that colloids may be filtered out of near-field water at the near-field/buffer interface [e.g. 80]. Work on the transport of colloids through bentonite has been undertaken internationally [e.g. 81,82] but, in general, such studies have been undertaken in the context of high level waste (HLW)/spent fuel (SF) disposal, under near-neutral conditions, rather than under high pH conditions typical of a cementitious near field/ADZ. Such work will not be discussed in detail in this report.



The current understanding of near-field colloid behaviour is summarised at the end of each of the relevant Sections that follow (2, 3, 4, and 5).

Based on the answers to the above questions at the time, approaches were developed to treat near-field colloids in two assessments of cementitious repository systems undertaken in the mid-1990s, Nirex 97 [36] and Wellenberg (Switzerland) [83]. These treatments are reviewed in Section 6.

## 2 Colloid generation in the near field

This Section reviews current understanding of colloid generation in the near field of a cementitious repository. The main sources of information come from laboratory experimental programmes that have been concerned with colloid generation, principally, from cementitious materials under consideration as backfill materials or waste encapsulation grouts. These will be the predominant materials in a cementitious repository in terms of volume and mass (see for example Figure 1.3) and were identified from early review studies as potentially important sources of near-field colloids [e.g. 8]. Further information is available from the results of colloid analyses of leachates from a number of equilibrium leach tests [23,30,31], which combined waste and cementitious materials, and from studies of the cementitious natural analogue site at Maqarin in Jordan [14]. Rather less information is available concerning colloid generation in the ADZ.

Key aspects of the study of colloid populations under simulated laboratory conditions and in natural systems in the field are the methods used for sampling and subsequent colloid analysis. Therefore, this Section includes a review of colloid analysis techniques. The review focuses primarily on those techniques which have been applied in experimental programmes to study colloid formation under near-field conditions, but also looks more widely to recent developments in colloid analysis that might be applied in future experimental programmes. The strengths and weaknesses of the various techniques are discussed and the types of information that can be obtained outlined.

A feature of colloid populations in shallow groundwaters, soils and surface waters is the association of inorganic colloid material with natural organic substances [84]. Indeed adsorption of organic materials onto mineral particles provides an important mechanism for colloid stabilisation in natural systems. Although the near field of a cementitious repository will be dominated by cementitious materials, the UK waste inventory contains a significant amount of organic material. This includes cellulosic materials (e.g. paper, cloth, wood), halogenated and non-halogenated plastics and rubbers, polymeric ion exchange resins, complexing agents (e.g. citric acid and picolinic acid), oils and other organic liquids [85]. In addition, polymeric materials are under consideration as waste encapsulants and the use of (organic) superplasticisers to improve flow characteristics and reduce water demand of cements is being considered in a number of programmes. This material, either as disposed or on degradation, will yield soluble species, some of which may be colloidal in size. In addition, soluble organic material may interact with solid surfaces including colloid surfaces. This latter aspect of colloid behaviour has received relatively little attention in work on colloid generation in the near field, but will be briefly discussed based on available information.

The authors are not aware of any published specific work on colloid generation from organic waste materials undertaken on radioactive waste disposal programmes. The emphasis of work on organic waste materials has been on the potential of either as-disposed materials or species formed on waste degradation to form complexants that may bind strongly with key radioelements enhancing their solubility and reducing their sorption in the near field (see for example [86, 87,88,89]). More recently, the potential formation of non-aqueous phase liquids from the degradation of organic materials has received attention [90]. (The potential for colloid entrainment in NAPLs phases will be discussed in sub-section 5.2.3.)

Laboratory studies on the Nirex research programme have identified the products of the alkaline degradation of cellulose (in particular isosaccharinic acid (ISA)) as potentially the most significant in affecting radioelement chemistry, not only because of the stability of the complexes that are formed but because of the large inventory of these wastes [91]. The effects of 'as-disposed' complexants or those generated from the long-term degradation of synthetic or natural non-cellulosic polymers are considered to be much less significant [91]. Likewise, the potential effect of organic waste-derived colloids on radionuclide mobility is likely to be small compared to the effects of small dissolved organic complexants, such as ISA, unless the colloidal material is significantly more persistent (*cf.* humic substances) under repository



conditions than small organic complexants, which may potentially be consumed by microbial or chemical processes. A more extensive review of the scientific literature concerning possible colloid generation from organic materials was considered beyond the scope of this report.

The Section is structured as follows. First, experimental approaches to studying colloid generation in cementitious systems in the laboratory will be reviewed (sub-section 2.1). Methods for characterising colloid populations formed will then be discussed (sub-section 2.2) and the results obtained on laboratory programmes will be summarised (sub-section 2.2.7). Studies of colloid populations in the natural cementitious analogue site at Maqarin in Jordan will be reviewed (sub-section 2.4). Studies of colloid generation in the ADZ will be discussed briefly (sub-section 2.5) and the understanding of the interactions of organic compounds with near-field colloids will be reviewed (sub-section 2.6). A brief overview will be given of current understanding of colloid populations in the far field (sub-section 2.7) to help put understanding of near-field colloids into a wider context. Finally, current understanding of colloid generation in the near field will be summarised in sub-section 2.8.

### 2.1 Colloid generation studies

#### 2.1.1 Materials

Experimental studies of near-field colloid generation published to date have been concerned principally with colloid generation from the cementitious materials under consideration as backfill materials or waste encapsulation grouts on national programmes, either on their own or, on occasion, in contact with simulated waste materials. As noted in Section 1.1, these materials vary both in their bulk chemical composition and in the composition of their porewaters on leaching, that condition the near field to high pH.

Since the early 1990s, near-field chemistry studies on the Nirex programme have focused on the properties of the Nirex Reference Vault Backfill (NRVB). This has included studies of radioelement sorption, solubility, cement leaching studies, microbial activity and studies of colloid generation. The NRVB is composed of a mixture of Ordinary Portland Cement (OPC), hydrated lime, limestone flour and water in the following proportions [92]:

OPC	450 kg m⁻ <sup>3</sup>
Hydrated lime (Ca(OH) <sub>2</sub> )	170 kg m <sup>-3</sup>
Limestone flour (CaCO <sub>3</sub> )	495 kg m <sup>-3</sup>
Water	615 kg m <sup>-3</sup>
Water/OPC	1.37 by weight
Water/solids	0.55 by weight

The NRVB is characterised by a high calcium content and a high initial Ca/Si mole ratio, with a significant excess of portlandite,  $Ca(OH)_2$  that will condition near field pH to about 12.5 for a very long period.

Typically, the material used in near-field colloid studies was taken from cubes or cylinders of material that after casting, hardening and demoulding, had either been wrapped in polythene and stored under controlled curing conditions (typically  $20 \pm 2^{\circ}$ C,  $85 \pm 5$ % relative humidity), or immersed in a bath of saturated calcium hydroxide solution open to air. This solution was used to minimise reaction of the cement with CO<sub>2</sub>, which will be referred to as carbonation. Only materials from the centre of cured samples were used in the experiments.

Some early work on the Nirex programme was undertaken to study colloid generation from crushed samples of two typical waste encapsulation grout compositions: 3:1 Pulverised Fuel Ash (PFA):OPC and 3:1 Blast Furnace Slag (BFS):OPC [27].



Work on the Swiss programme has focused on the Nagra Monokorm mortar, M1, which is a *"like-grained mix prepared from quartz aggregates and Portland (Sulfazem PZHS) cement*". The aggregate material is a commercial product with grain size of 2-4 mm. The recipe for mortar M1 has the following composition by weight [37]:

Cement : water : aggregate = 1.00 : 0.4 : 5.33 (i.e. water/solids = 0.06)

The M1 material is characterised by a much higher silica content, and lower calcium and water content than NRVB. It is designed to be a highly permeable material with a large pore size. Porosity is about 27%.

The material used in colloid generation experiments was cast in cylinders and typically cured for 2 months at 90% relative humidity before being crushed for use.

Work undertaken by AEA Technology (AEAT, now Serco) for CRIEPI on the Japanese programme focused on two cement formulations: a 9:1 BFS/OPC grout and a lower-pH cement referred to as High Flyash and Silica fume-content Cement (HFSC). The approximate solid ratios are [93]:

Portland cement : Flyash : Silica Fume = 2 : 2 : 1, Ca/Si = 0.83

As a result of a pozzolanic reaction between the OPC and silica content of both HFSC and BFS/OPC, no free portlandite  $(Ca(OH)_2)$  is expected in their hydrates; after initial leaching of alkali metal hydroxides (KOH, NaOH), the pH of the cement porewater will be conditioned to lower, but still alkaline, pH by the dissolution of calcium silicate hydrate (CSH) phases.

#### 2.1.2 Experimental conditions

The combination of high pH (greater than pH 12 for NRVB and cementitious grouts) and significant dissolved calcium concentrations (usually greater than  $2 \times 10^{-3}$  mol dm<sup>-3</sup>) in cement leachates means that experiments with cementitious systems are very susceptible to the presence of carbon dioxide. The generation of artefact colloids due to CO<sub>2</sub> uptake and precipitation of CaCO<sub>3</sub> is an ever-present risk unless suitable controls are put in place and maintained. In designing laboratory experiments to study colloid generation from cementitious systems, it is important that CO<sub>2</sub> is excluded at all stages from the preparation of leaching waters, through leaching, sampling and the preparation of specimens for analysis. This is achieved by carrying out the experiments in a controlled atmosphere glovebox containing O<sub>2</sub> and CO<sub>2</sub>-free nitrogen, although other gases such as argon may be used. On the Nirex programme, nitrogen-atmosphere gloveboxes where O<sub>2</sub> concentrations were maintained below 100ppm and CO<sub>2</sub> concentrations would be very low (assumed to be less than a few ppm at levels in the supplied nitrogen) were used. On the NAGRA programme, low O<sub>2</sub> and CO<sub>2</sub> controlled N<sub>2</sub>-atmosphere gloveboxes were used (<2ppm O<sub>2</sub>, CO<sub>2</sub>) [9].

The precipitation of  $CaCO_3$  has proved to be a significant problem in a number of studies, and indeed may have been an unrecognised problem in others. The formation of artefact colloids, at any stage of the experiments, can swamp or mask the true colloid populations, distorting the results of the experiments, and may lead to significant over-estimation of the true colloid populations. This indeed was the case in early studies undertaken for Nirex [27] (see discussion in [19]); those results affected are not considered here.

Three types of experiments have been used to study the formation of colloids under simulated near-field conditions in the laboratory. These are:

- batch leaching experiments;
- column experiments; and
- equilibrium leach tests.



Each of these three approaches is outlined in the sub-sections below.

#### 2.1.3 Batch leaching experiments

The most commonly used experiments to study the formation of colloids under near-field conditions have been batch leaching tests in which cured cementitious materials in the form of granules or intact samples have been leached in a solution of selected composition (ranging from demineralised water to simulated saline groundwaters). The materials may be leached under either essentially undisturbed conditions or with regular or occasional agitation. The solution phase is sampled periodically and the colloid component of the solution is analysed using one or more characterisation techniques (see sub-section 2.2).

In batch experiments, the solid to liquid (S/L) ratio can be varied to see the effect of this parameter on the colloid concentration. Typically, S/L ratios used have ranged between 1:5 and 1:100, although these values are always significantly lower than values that would be realistic of repository near-field conditions. In some studies, the effect of temperature has been investigated also. However, the potential for artificial colloid formation on cooling elevated temperature leachates to room temperature for analysis (due to nucleation and growth from solutions that may become supersaturated with respect to solid phases on cooling), must be recognised.

An overview of the batch leaching studies described in the literature and discussed in this review is provided in Table 2.1. More specific details of each batch leaching study are outlined in sub-section 2.2.7. In most cases, with the exception of the early UKAEA work [25,26], the leaching experiments and all leachate handling were undertaken throughout in nitrogenatmosphere gloveboxes.

#### 2.1.4 Column experiments

Unlike static batch experiments, column experiments are often perceived as being more realistic because transport processes can be examined at the same time as, for example, leachate-rock or radionuclide-rock interactions (e.g. 94,95). Arguably, however, column experiments are less appropriate than batch experiments for examining the generation of near-field colloids owing to the significantly higher flow rates that are required to perform experiments over laboratory timescales. Such high flow rates may apply erosional forces that are not representative of the near-stagnant conditions in a GDF.

Nevertheless, it is worth looking at one recent, large-scale column experiment that included a study of near-field colloids as a sub-task within the main project. COLEX (COLumn EXperiments) I [96] had the primary goal of studying coupled gas and water transport in Nagra's M1 mortar; the assessment of colloid populations in a few leachate samples was included in the middle of the experimental run [9, 97].

#### 2.1.5 Equilibrium leach tests (ELT)

Sometimes referred to as 'black box' experiments, ELTs are designed to simulate the situation in a radioactive waste repository after groundwater has penetrated the engineered barriers (i.e. the vault backfill, the waste containers and the wasteform). These experiments usually contain a mixture of key near-field components: simulated (or real) waste, spiked or contaminated with key radionulcides, cementitious grouts and/or backfill materials, container and a simulated groundwater. The experiments may be run for a number of years, at ambient or elevated temperature, under static conditions to simulate the low flow rate in a repository, and are sampled periodically to determine the evolution of the porewater chemistry, rates of gas release and the solubilities of radioelements, etc. Detailed post-leaching examination of the materials can be undertaken during the dismantling of the tests

In this report, two different suites of ELTs that incorporated colloid analysis are discussed.



### Table 2.1 Summary of batch leaching experiments to study colloid formation from cementitious materials reported in the literature

Programme and contractor	Cementitious materials and form	Leach waters	Temperatures	Solid to liquid ratios	Duration	Comments
UK DoE/CEC, UKAEA [25.26]	Monoliths of OPC,	Distilled water	Ambient, 60°C and 90°C	1:25 to 1:31; also 1:250 and 1:2500	Up to 356 davs	Static leach tests, limited experimental details: no
	1:1 and 5:1 PFA/OPC,			for OPC only		attempt to quantify colloid concentrations
	3:1 and 9:1 BFS/OPC					
Nirex, AEAT [27] see also [19]	Crushed NRVB	Demineralised water	Ambient, 60°C and 80°C	1:5, 1:10 and 1:50	1 week and 5 months	Static leach tests, results affected by artefact colloid formation during specimen preparation for analysis
	Crushed 3:1 PFA/OPC Crushed 3:1 BFS/OPC	NRVB-equilibrated water and simulated saline NRVB-equilibrated water	Ambient and 80°C	1:5 and 1:50	1 week	Static leach tests; results for BFS/OPC, but not PFA/OPC, affected by artefact colloid formation
Nirex, AEAT [19]	Crushed NRVB	Demineralised water	Ambient	1:5, 1:10 and 1:50	41 days	Static leach tests
Nirex, AEAT [19,28,29]	NRVB monoliths	Demineralised water	Ambient	Initially 1:5.25, 1:10 and 1:42.5	Up to 34 months	Periodic sampling of static tests
Japan, CRIEPI/AEAT [98]	Crushed HFSC	Low-salinity groundwater	Ambient, 60°C	1:5, 1:50 and	2 months	Static leach tests; results for BES/OPC affected by
CRIEFI/AEAT [90]	Crushed 9:1 BFS:OPC			1.100	months	artefact colloid formation
Nagra, Switzerland, PSI [9,18,97]	M1 mortar, 2-4mm grains Quartz aggregate, 2-4mm grains	Young cement pore water, artificial cement pore water (ACW) and Na-ISA in ACW	Ambient	1:10	Up to 330 days	Agitated twice daily by end over end mixing; analysis samples taken after 1 min, 24 hrs and up to 200 days standing


In the first, BGS, on behalf of Nagra undertook a seven year (1988 to 1994) experimental study to investigate the gross effects of microbial activity on repository geochemistry, radionuclide sorption and the integrity of the repository EBS materials and host rock [99, 100, 101]. Although colloids were not the principal concern of these 'black-box' microcosm experiments, samples were analysed also for colloid populations and chemistry.

In the second, AEA Technology (AEAT), on behalf of Nirex, carried out a seven year programme (1992 to 1999) where the principal near-field components (waste, encapsulation matrix, container and backfill) of an ILW repository were equilibrated with the aqueous phase under static conditions [102]. Here, the principal objective of the tests was to measure the resulting solution concentrations of key radionuclides. In addition, the tests provided a unique opportunity to investigate the formation of colloids and the association of radionuclides with colloids under simulated repository conditions. Colloid and activity analyses of leachate samples from the tests were undertaken following their destructive decommissioning [23,30,31].

#### 2.2 Colloid characterisation methods

A range of analytical methods are available to study the concentrations, compositions and particle size distributions of colloidal particles in environmental samples. The discussion in this Section will focus on the application of those methods that have been used to date on the UK, Japanese and Swiss programmes to characterise near-field colloids. These are:

- Transmission electron microscopy (TEM) coupled with energy dispersive X-ray analysis (EDX);
- Scanning electron microscopy (SEM) coupled with EDX;
- Photon correlation spectroscopy (PCS, or dynamic light scattering); and
- Single particle counting (SPC).

The strengths and weaknesses of each of these techniques and the types of information that can be obtained are outlined in the sub-sections below.

It should be noted however that not only have the above techniques seen significant advances in instrumentation over the last decade but a range of new techniques have also been developed that may potentially provide benefit for the study of colloid populations in future NDA RWMD programmes. These 'new frontiers' in colloid characterisation are outlined in Appendix 1.

#### 2.2.1 Transmission Electron Microscopy

TEM techniques have long been used to study colloidal systems and can potentially resolve features down to a few nm in size. However, a significant drawback of the technique is that the preparation of suitable specimens for quantitative analysis of dilute colloidal dispersions, free from artefacts, is difficult and requires considerable operator skill and clean conditions. This is particularly true when all solution handling and specimen preparation (until dry) needs to be undertaken inside a nitrogen-atmosphere glovebox.

TEM analysis requires the preparation of ultrathin samples of material in or on a matrix that is essentially transparent to the electron beam. For the analysis of colloidal particles, this requires either embedding the particle in a resin followed by the cutting of ultrathin sections (based on methods developed for studying biological structures) or the deposition of particles onto a carbon film (which may be either supported or unsupported). A review of colloid specimen preparation methods is given by Perret *et al.* [103].



One of the most widely-used specimen preparation methods for studying dilute colloid systems are ultracentrifugal deposition techniques such as that developed by Nomizu *et al.* [104], which was adopted by AEAT and used for work on both the Nirex and Japanese programmes. The technique involves depositing colloidal particles from a dispersion onto a carbon-coated copper grid using an ultracentrifuge. Particle adhesion to the grid can be improved by activating the grids in an ion beam (which makes them hydrophilic) prior to deposition. The grid is supported in the colloidal dispersion above the base of the centrifuge tube on a stub with a capping ring. 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 quantitatively onto the carbon film.

To minimise the formation of salt particle artefacts from the original leachate solution on drying, the grids may be washed *in situ* in the centrifuge tubes using dilute electrolyte solution (to maintain particle adhesion) with pH above 11 (to avoid particle dissolution). Washing is particularly important if leachates in saline waters are being studied.

It is good practise to prepare blank grids using portions of the leachate solution from which the colloid population has been removed, e.g. by passing through a 30,000 nominal molecular weight cut-off filter, for comparison with the original leachate. This provides a measure of the particle background arising from contamination (during fabrication, activation and handling) and drying artefact formation. Such a background was always found to be present in the TEM studies of cementitious leachates undertaken by AEAT, often dominated by a population of very small (<10 nm) artefact particles and crystals. For this reason, particles less than 15 nm in size were excluded from the colloid analysis.

Modern TEMs (and SEMs) are equipped with digital cameras that allow numerous high-quality images of colloidal specimens to be recorded at different resolutions (e.g. Figure 2.1). Image analysis tools may be used to assist particle number and size distribution analysis. In the past, instruments were equipped, usually, with high quality 'cut-plate' photographic systems, and analysis was undertaken manually on prints, a much-more laborious process. This was the case on near-field studies undertaken by AEAT for Nirex [19,28] and CRIEPI [98] where TEM was used to for colloid analysis.

It is important when estimating colloid populations from electron micrographs that a sufficiently large number of particles are measured from a number of areas of the specimen to give values that are statistically-representative. This may be difficult to achieve in cases where colloid concentrations are very low. Indeed, because a point of focus is required for imaging, where coverages are low, there may be an inherent bias to photograph regions with higher particle numbers. For the measurement of size distributions, particles are measured at a number of image resolutions to resolve different size ranges of the population.

In the case of the TEM studies undertaken by AEAT, the number of electron mirographs that could be recorded from each specimen was limited by the number of plates that could be exposed in a session (up to 36). Therefore, imaging was selective rather than random with a bias to record high quality images from a small number (usually 1 or 2) of grid squares per specimen that showed uniform particle distributions. Thus there is an uncertainty concerning how statistically-representative the measured colloid populations were of the original dispersions. For this reason, it was very difficult to estimate uncertainties associated with the number concentrations, and in general these were not evaluated. Thus the results should be viewed as semi-quantitative.

Nevertheless, the methodology outlined above was tested on the Nirex programme and found to be essentially quantitative when used to estimate the colloid concentrations for dilute dispersions of model spherical silica colloids [19].



Figure 2.1 TEM micrographs of particles imaged from lake water and sediments. (a) Globules found in associated creek sediments. (b) Algal cell (center) surrounded by a large number of zinc containing particles. (c) Bacterial cells in the water column. (d) Diatom frustule found in the water column. (e) Globules collected from sediments at associated creek outlet (from [105]).

#### 2.2.2 Scanning Electron Microscopy

In general, scanning electron microscopes tend to be more widely available than TEMs and, sample preparation is in many respects, considerably easier. However, the inherent resolution of SEM is not as good as TEM, limiting the smallest-sized particles that can be measured. The minimum particle size measurable (usually > 30 nm) may be limited also by the specimen preparation method.

Colloid analysis by SEM requires deposition onto a suitable substrate, followed by sputter-coating with a conducting film of gold or carbon (gold is usually better with filter substrates). For quantitative analysis, this is most readily achieved by deposition onto a membrane filter mounted within a filtration cell. The most suitable substrates are 0.05 µm track-etched membrane filters which have a flat surface and very regular pore size. In this case, particle size distributions can be measured down to about 50 nm. Smaller particles that are deposited on the filter may potentially be measurable, depending on the resolution of the SEM, however their concentration cannot be measured quantitatively.

A particular advantage of this preparation method is that the filtration cell can be pressurised directly with nitrogen and the filter can be washed readily and partially dried *in situ*. As a result, the technique has been found to be less susceptible to artefact formation than the TEM specimen preparation method outlined above. In addition, a much wider range of leachate volumes can be used in sample preparation than with the TEM method, allowing more dilute dispersions to be characterised; indeed with preliminary information, the volume can be selected to give the optimum coverage for particle analysis.

Two types of images can be collected in an SEM, secondary electron (SE) images, which show topographic contrast, and backscattered electron (BSE) images, which show atomic number contrast. The latter can be used to highlight particles rich in heavier elements (e.g. Fe, Sr-rich, U) against a background of lighter element particles (e.g. Al, Si-rich).

SEM was used to measure colloids in cementitious leachates in early UKAEA work [26] and on the Nirex programme [29,30,31]; an SEM suitable for handling active samples was used to study active leachates collected from two equilibrium leach tests [30] although the resolution of this instrument was significantly poorer than non-active instruments.

#### 2.2.3 Energy Dispersive X-ray Analysis

EDX systems are common accessories to both TEM and SEM instruments and enable the compositions of individual particles or groups of particles to be determined, depending on the size and distribution of particles under examination. The electron beam is focused to a spot on a particle or group of particles and the characteristic X-rays emitted by the elements are detected using an energy-discriminating X-ray detector. The minimum energy detectable is dependent on the window material. The use of ultra-thin Mylar windows or can allow detection of low atomic number elements including carbon and oxygen. However, their detection in the sample requires that they are not components of the matrix or substrate.

In general, the X-ray spectrum is considered to give a semi-quantitative measurement of particle composition, which, in general is adequate for most purposes. Typically single particle analysis can be undertaken on particles greater than about 500 µm in size by SEM, somewhat smaller by TEM. Usually, owing to time constraints, the number of particles that can be studied is limited and will not give a statistically representative distribution of particle composition. However, the 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, for example.



EDX has been used to identify particle compositions in all SEM/TEM studies undertaken by AEAT on the Nirex and Japanese programmes and by SKB for studies in their Aspö URL (see Figure 2.2).



Figure 2.2 SEM micrographs (to the left) of the 0.4 μm membrane (magnification = ×10,000) and the EDS spectrum (to the right). a) The sample from borehole SA2273A contains some large particles but also some small aggregates, the EDS spectra indicate the presence of Fe, Ca, Si (Au is a method artefact; Cl is due to saline groundwater precipitation). b) The sample from borehole HA2780A shows a more homogeneous size distribution but similar elemental peaks (from [68]).

#### 2.2.4 Single Particle Counting

Single Particle Counting (SPC) techniques have been used at PSI to characterise colloid populations in cementitious leachates in terms of particle concentration and size distribution [9]. These techniques operate on the principle that a particle transported in a fluid through a laser beam will scatter light in direct proportion to its size and through an angle that is larger the smaller the particle.



The instrumentation used at PSI involves the gradual injection of a water sample into a carrier of high purity demineralised water which is pumped at high flow rate through one or more particle sensors. Particle sensors of varying type may be used. In general, the pulses of scattered light are recorded by photodioide detectors positioned at 90° to the incident laser beam. Provided the dispersion is sufficiently dilute (or diluted) to ensure detection of single particles, size information from individual particles can be acquired on a fast and continuous basis. The method has the particular advantage that water samples can be analysed directly without requiring intermediate specimen preparation.

Because the SPC method involves counting of individual particles, it has the potential to measure very low number concentrations with reasonable accuracy. In practice, however, detection limits will be determined by the background levels of particles in the carrier water and the maintenance of cleanliness throughout the flow systems. At PSI, the background was found to range from about  $10^6$  to  $5 \times 10^7$  particles dm<sup>-3</sup> depending on the size range detected by the sensors.

#### 2.2.5 Photon Correlation Spectroscopy

PCS, also known as dynamic light scattering, is used to measure the diffusive motion of particles dispersed in a liquid from which particle size information can be obtained. A dispersion of interest contained in a cuvette is mounted in a thermostatted vat of liquid and illuminated with a focused laser. Owing to the Brownian motion of the particles, interference between scattered light produces fluctuations in the intensity with time, which are detected, usually with a photomultiplier. The smaller the size of the particles, the faster they diffuse and the more rapid are the fluctuations in intensity. Data are collected at a chosen angle to the incident beam in the form of an intensity autocorrelation function, which correlates temporal fluctuations in the scattering intensity. For a sample of non-interacting monodispersed particles it can be shown [106] that the normalised autocorrelation function, decays exponentially with coefficient that is proportional to the particle translational diffusion coefficient, *D*. The smaller the particles, the faster the rate of decay. For the case of spherical particles, a hydrodynamic particle size, *d*, can be calculated from *D* by applying the Stokes-Einstein equation:

$$d = \frac{kT}{3\pi\eta D}, \qquad (2.1)$$

where *k* is the Boltzmann constant, *T* is temperature and  $\eta$  is the solvent viscosity.

For the case of non-uniform or polydisperse samples it is generally assumed that the autocorrelation function is given by the superposition of decays arising from each particle size at the given scattering angle. Suitable analysis of the shape of the autocorrelation function can yield information about particle size distributions. A number of analysis methods are available [e.g. 107,108]. The scattered intensity from particles of different size also varies with angle from the incident beam – with increasing angle the intensity decays inversely with size (static light scattering or Mie scattering). Therefore, measurement of autocorrelation functions at different angles can help to resolve different size components of a complex size distribution.

In principle, PCS can be used to study both the steady-state size distribution of particles in a water sample and the kinetics of aggregation of particles through changes in the size distribution with time. Although PCS has been used to characterise colloid populations in natural water systems [109], the technique has a number of constraints that limit its applicability to very dilute colloidal systems that are typical of groundwater samples and cementitious leachates. First, very high powered dedicated lasers (e.g. 1W) are required to measure sufficient scattering for analysis from dilute colloidal systems. Indeed for very dilute samples, pre-concentration of colloid populations may be required. Secondly, because scattering intensity is proportional to the sixth power of the radius (for particles smaller than the laser wavelength), the detection of particles less than 50 nm in size is very difficult at environmental

concentrations, particularly in the presence of even small fractions of larger particles that may dominate the scattering. To characterise such polydisperse samples, fractionation of the sample may be required [110]. At a minimum, it is customary to pre-filter water samples (e.g. through a 5 µm pore-size filter) prior to PCS analysis to remove particulates.

In terms of near-field colloid studies, PCS has been used principally in aggregation studies of stimulant colloids at significantly higher particle concentrations than have been measured in cement leachates to date. Such studies are discussed in Section 3.

#### 2.2.6 Colloid concentration and fractionation techniques

Colloid concentration techniques have been used on the Nirex programme for the preparation of both groundwater and near-field colloid concentrates to enable further experimentation or analysis (see Section 4). Fractionation techniques may also be of value on a future colloid programme. Examples of both types of methods are discussed below.

#### a) Ultrafiltration

Owing to the low colloid concentrations measured in groundwater systems and also found in cementitious leachates (as discussed in sub-section 2.2.7), concentration of the colloid populations may be required for more detailed analysis (such as uranium-series isotope analysis) or their use in further experiments. Colloid concentration techniques are commonly based on ultrafiltration methods where particles are retained on filter membranes of suitable pore-size. The term ultrafiltration is used where the pore size is sufficiently fine that pressure or suction needs to be applied to force the solution phase, including particles smaller than the pore-size, through the filter.

Sequential filtration of solutions through filters with progressively smaller pore size (sometimes referred to as cascade filtration) can be used as a colloid fractionation technique. In general, colloid filtration should not be regarded as a straightforward sieving process, however [110]. Filtrate populations may be affected both by the loss of particles smaller than the pore size by sorption to filter surfaces and by pore blockage due to the formation of filter cake if the amount and/or of filtered material is too large. These limitations need to be recognised and their influence assessed for the system under investigation. Their effects can be minimised by decreasing the thickness of the (stagnant) diffusion layer above the membrane either by stirring the bulk solution or by using tangential flow filtration; they can also be minimised by using lower flow rates.

For work at high pH, filters made of alkali-resistant materials such as polysulphone or polypropylene are required. In preliminary work for sampling at Maqarin, the potential retention of colloids to the two alkali-resistant filter types was checked in the laboratory prior to their use in the field. Colloid analysis following filtration found no evidence for retention of the standard colloids used (see Appendix 1 of [14] for further details).

Figure 2.3 shows an arrangement for in-line sampling of a groundwater, as used at the Maqarin analogue site in Jordan (see sub-section 2.4 for further details). In this example, water is collected in 50 cm<sup>3</sup> capacity filtration cell after being passed through a 1  $\mu$ m nominal pore size pre-filter (to remove any large particles). When the cell is full, the valve can be switched to the gas line and the water is pushed through the filter by the overpressure of high-purity nitrogen.

Tangential flow ultrafiltration has been used extensively to produce colloid concentrates and colloid-free ultrafiltrates of groundwater samples [e.g. 52,111,112]. It was also used to prepare a colloid concentrate from NRVB leachate for use in sorption experiments (see sub-section 4.3). The technique can be applied either directly in the field or (on a smaller scale) in the laboratory. In general, a large volume (many tens to hundreds of litres) can be circulated through a tangential flow ultrafiltration rig under a nitrogen atmosphere and colloids are retained in a litre



or so of concentrate. On completion of the concentration step, the concentrate is recovered and the filter can be washed with acid solutions to recover retained material for analysis.

For work with cementitious leachates, all tubing, valves, sample bottles, connectors, etc. should be alkali-resistant. All the apparatus used should be acid washed, rinsed in distilled water, dried in a laminar flow hood and finally packed in polythene bags until use to minimise contamination.



Figure 2.3 Example of an in-line filter cell, in this case for field sampling (from [14])

#### b) Field-flow fractionation

Recently, Flow Field-Flow Fractionation (FFFF) techniques have been utilised to fractionate colloidal dispersions. Currently, 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  $\mu$ m. Fractionation 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 (Figure 2.4) – 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 (Figure 2.5). 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 and are caught in the faster parts of the laminar flow and so are eluted more rapidly than larger colloids.

As with the two methods discussed above, the samples produced by AF4 are then passed on to a wide range of analytical techniques (see below). An advantage of AF4, however, is that many of the analytical methods can be effectively directly coupled to the sample stream (e.g. [113]), so minimising potential sampling artifacts. Potential drawbacks include reaction of the colloids in the cross flow, a potentially significant problem when studying some types of near-field colloids.



#### c) Other fractionation techniques

Other hydrodynamic based separation techniques such as split-flow thin-cell (SPLITT) fractionation has been used infrequently for separating environmental colloids but it appears to be a promising fractionation method for sizes less than  $1\mu$ m (although centrifugal SPLITT can perform separations down to <0.1 $\mu$ m [114]). The technique may also be developed as a preseparation method for subsequent colloidal fractionation and analysis. As this methodology is in its infancy, it will not be discussed further here.



Figure 2.4 Schematic illustration of the general separation principle of Field-Flow Fractionation (courtesy of Postnova Analytics)



Figure 2.5 Separation principle of Asymmetric FFFF (courtesy Watt Technology Corporation)

#### 2.2.7 Interpretation of 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 [115]:

$$n(d_{\rm p}) = \left(\frac{\Delta N}{\Delta d_{\rm p}}\right) = Ad_{\rm p}^{-\beta}, \qquad (2.2)$$

where  $n(d_p)$  is the distribution function for particle size,  $d_p$ ,  $\Delta N$  is the number of particles with a diameter in the size interval  $\Delta d_p$ ; A and  $\beta$  are constants. This relationship appears to hold for particles in groundwater systems down to at least 100 nm in size (based on [55]) and up to 100 µm in surface waters [115], displaying a linear region in a log-log plot of  $\Delta N$  versus size class with slope  $-\beta$ .

The value of  $\beta$  provides an insight into how the size distribution has evolved with time. When particles are produced by erosion,  $\beta = 4$  [55]. However, when nucleation or aggregation occurs, the values of A and  $\beta$  will be modified. Aggregation will favour the formation of larger particles over smaller ones and will result in a reduction in  $\beta$ ; nucleation of new particles will tend to increase  $\beta$ . In general, environmental samples are often found to have  $\beta$  in the range 2-5, and close to 4 in many cases [115].

Thus, determination of particle size distributions using appropriate size discriminating colloid analysis techniques can (in principle) provide additional insight into the nature of the colloid population. Near-field colloid size distributions determined by PSI using SPC and latterly on the Nirex programme by AEA Technology using SEM/TEM techniques have been interpreted, where possible, using equation 2.2.

#### 2.3 Measured population ranges, compositions and size distributions of near-field colloids

As recently as 2004, an US report [116] noted that the long-term, *in situ* behaviour of cement grouts is not well understood and that cement degradation pathways are "...*still not fully understood*". To some extent, this uncertainty is clearly reflected in the colloid generation experiments outlined in sub-section 2.2, above, with a range of basic approaches. This makes intercomparison of the data on colloid populations and types rather complex as there are clear method-induced differences in measured colloid populations [117]. Nevertheless, it is worth looking at the existing data for near-field colloid populations and masses and comparing these with data for (natural) far-field colloids to give some sense of the relative masses involved. Note that although the current NDA reference design for a cementitious repository does not include bentonite, many designs do [e.g. 17], so bentonite colloids will also be considered for completeness.

#### 2.3.1 Cementitious colloids

Available data on cement colloids are presented in Table 2.2 and the data show that cementderived colloid populations are likely to be very low (about 0.1 mg dm<sup>-3</sup>). However, as noted in section 2.2, the experimental set-up and methods used most certainly have a significant impact on the populations measured so this will be investigated further here. A variety of methods has been employed and will be summarised here to aid interpretation.



#### a) Early studies (UK DoE/CEC)

In early work undertaken for UKDoE/CEC [25,26] leaching experiments were carried out on a range of cement formulations (OPC only, 3:1 and 9:1 BFS/OPC mix and 3:1 and 9:1 PFA/OPC mix), which were prepared in the form of cylindrical pellets and cured at room temperature for a minimum of 28 days (with exclusion of  $CO_2$ ). Leaching was carried out with N<sub>2</sub>-purged distilled water in borosilicate glass flasks (and later in inert plastics), sealed to exclude  $CO_2$ , at three temperatures: ambient, 60° and 90°C. After prolonged periods, deposits with a white fluffy appearance were observed adhering to the flask walls. Samples of the leachates and deposits were filtered through filters of various pore-sizes; filtered solutions were examined by PCS (initially) and the particles retained on filters were examined by SEM. However, most of the particles in the colloidal size range. No attempt was made to quantify colloid (or particulate) populations or size distributions in this study. Therefore, these experiments are viewed as providing a demonstration of the potential for colloid formation from cementitious systems.

Particulates with a size greater than 1 $\mu$ m were detected by PCS in OPC leachates at 25°C after 14 days leaching. Particulates with a range of sizes and morphologies were retained on filters as observed by SEM. Most particles were composed of aggregates. For example, aggregates of spherical particles of between 1 and 5  $\mu$ m in size and of rod-like particle with dimensions 0.8 x 0.1  $\mu$ m were observed from OPC 25°C leachates about 150 days old. Some of the spherical particles themselves appeared to have been produced by the build-up of layers. Similar spherical particle aggregate structures were observed after leaching for only 16 days at 60°C. Limited EDX results indicate particles composed of Ca only (probably calcite) and CSH gel. X-ray diffraction analysis of deposits indicated the presence of amorphous CSH-gel. Particulates were less numerous in BFS/OPC 9:1 and 3:1 leachates.

On the basis of these results the following mechanism was proposed for particulate formation in cement. Initially, the calcium concentration rises rapidly due to dissolution of calcium hydroxide in the cement. The leaching of silicon is slower, but over longer periods the saturation limit of a CSH gel phase is reached in the leachate and the onset of colloid formation occurs. Further leaching probably results in particle growth and aggregation (due to the high ionic strength). The latter processes are accelerated at high temperatures resulting in substantial deposits of CSH gel phases.

In general, the particulates observed in these studies are too large to be considered mobile in the near-field porewater. The appearance of the aggregate particle structures provided circumstantial evidence for the transient presence of particles of colloidal dimensions (1 - 1000 nm), but a distinct fraction of particles of smaller size was not distinguishable.

#### Table 2.2 Comparison of existing data on near-field cementitious colloids

Study	Methodology	Colloid Population Coll (dm <sup>-3</sup> )		Colloid Concentration (mg dm <sup>-3</sup> )	Comments		
3:1 PFA/OPC granule leaching experiments [27] plus see discussion in [19]	Leaching of crushed PFA/OPC in NRVB- and simulated saline NRVB- equilibrated water at solid to liquid ratios of 1:5 and 1:50 for 1 week	10 <sup>10</sup>	<sup>0</sup> -2 × 10 <sup>11</sup>	-	Colloid sampled from leachate with minimal agitation of sample. TEM grids were dried in air but do not show evidence of Ca-rich artefact particles observed on contacting NRVB leachates with air.		
NRVB granule leaching experiments [19]	Leaching of crushed NRVB in demineralised water at solid to liquid ratios of 1:5, 1:10 and 1:50 for 41 days at ambient	4 - $5 \times 10^{10}$ (all three S/L ratios)		4 - 5 $\times$ 10 <sup>10</sup> (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 [19, 28]	Leaching of cut square-faced sticks of cured NRVB in demineralised water at initial solid to liquid ratios of 1: 5.25, 1:10 and 1:42.5	36 days $<10^{11}$ 12 mths $<7 \times 10^{10}$ 18 mths $<1.1 \times 10^{11}$ (all three S/L ratios)		_	Formation of very small (<50 nm) artefact particles on TEM grids effectively masked the NRVB-derived colloid populations. Estimated populations are upper limits that include artefact particles. The NRVB- derived colloid populations were considered to be less than 10 <sup>10</sup> dm <sup>-3</sup> .		
Continuation of NRVB monolith leaching [29]	After 24 months S/L ratios were 1:4.4, 1:8.8, 1:34.8	S/L 4.4 8.8 34.8	$\begin{array}{l} 3.6 \pm 1.4 \times 10^{10} \\ 8.8 \pm 2.8 \times 10^{10} \\ 5.6 \pm 5.0 \times 10^{10} \end{array}$	-	Populations for > 50nm size fraction. Analysis by SEM allowed larger sample volumes to be used for specimen preparation and reduced problems associated with artefact particle formation. Artefact particle levels reduced to values equivalent $10^{10}$ dm <sup>-3</sup> or less depending on sample volume used.		

Study	Methodology	Colloic	l Population (dm <sup>-3</sup> )	Colloid Concentration (mg dm <sup>-3</sup> )	Comments
NRVB monolith leaching (continued)	After 31 months S/L ratios were 1:2.8, 1:6.5, 1:23.9 After 34 months S/L of initially 1:5.25 experiment was 1.7	S/L 2.8 6.5 23.9 1.7	$5.1 \pm 0.5 \times 10^{10}$ $1.6 \pm 0.3 \times 10^{10}$ $1.0 \pm 0.3 \times 10^{10}$ $3.2 \times 10^{9}$		Results after 31 months potentially enhanced due to sampling by decanting. Results are for 5 µm pre-filtered samples.
CRIEPI batch leaching studies [98]	Pulverized samples of High Flyash and Silica fume-content Cement (HFSC) hydrate were leached in low-salinity groundwater at three solid-to-liquid (S/L) mass ratios (1:5, 1:50 and 1:100), and two temperatures (20 and 60 °C) for durations of nearly 2 and 8 months.	10 <sup>11</sup> – 10 <sup>12</sup> (for 1:50 and 1:100 S/L ratios)		-	HFSC-derived colloid stability is due to a high negative zeta potential at alkaline pH values, combined with Ca concentration below the critical coagulation concentration. A preliminary interpretation of HFSC- colloid stability based on DLVO theory provides a semi-quantitative explanation of the dependence of colloid populations on the S/L ratio in the leaching experiments
PSI batch leaching experiments [9]	Leaching of crushed PZHS (High Sulphate Resistance Portland Cement.) M1 monocorn mortar (2-4mm diameter) or quartz aggregate with cement pore waters, solid:liquid ratio of 1:10	M1 0.3 Q 0.7 M1 2.4 Q 1.8	$3 - 1.1 \times 10^{11}$ - 3.0 × 10 <sup>11</sup> 4.0 × 10 <sup>10</sup> 7.5 × 10 <sup>9</sup>	-	'Total colloid' concentration measured 1 minute after end-over-end mixing of a batch system. Experimentally defined colloid diameter ≥ 100nm. 'Undisturbed colloid' concentration measured after leaving batch system undisturbed for 24 hours. Experimentally defined colloid diameters between 100nm and 1000nm. Particles >1000nm diameter settle out during the 24 hour pause.

Study	Methodology	Colloid (	Population dm <sup>-3</sup> )	Colloid Co (mg	oncentration dm <sup>-3</sup> )	Comments
PSI batch leaching experiments (continued)		M1 3.2 2.2 Quartz 2 1	$2 \pm 2.4 \times 10^{8}$ $2 \pm 0.8 \times 10^{8}$ $2.4 \pm 1.5 \times 10^{8}$ $1.9 \pm 1.4 \times 10^{8}$			'Steady state colloid' concentration measured after leaving batch system undisturbed for 150 - 200 days (following agitation for 180 – 330 days). Experimentally defined colloid diameter >100nm<1000nm. No significant differences between M1 and quartz aggregate leachates.
PSI batch leaching experiments in presence of ISA [9]	Leaching of crushed PZHS (High Sulphate Resistance Portland Cement.) M1 monocorn mortar (2- 4mm diameter) or quartz aggregate with cement pore waters and Na- isosaccharinic acid (ISA), solid:liquid ratio of 1:10	$\begin{array}{c} \text{M1 } 2.2 \pm 0.3 \times 10^{11} \\ \text{Quartz } 3.4 \pm 0.2 \times 10^{11} \\ \\ \text{M1 } 6.2 \pm 0.2 \times 10^{10} \\ \text{Quartz } 1.4 \pm 0.2 \times 10^{10} \\ \\ \\ \text{M1 } 8.0 \pm 3.5 \times 10^{8} \\ \\ \text{Quartz } 4.5 \pm 2.6 \times 10^{8} \end{array}$		-		'Total colloid' 'Undisturbed colloid'
						'Steady state colloid' No significant differences with ISA present.
PSI column experiments [9]	Leaching of crushed M1 mortar in a column with cement pore waters (Mean concentrations at top and <i>bottom</i> of column) Sample 1 (week 1) average	1-1000 nm 1.8 × 10 <sup>14</sup> 3.0 × 10 <sup>14</sup>	50-1000 nm 7.1 × 10 <sup>9</sup> <i>1.8 × 10<sup>10</sup></i>	1-1000 nm 0.019 <i>0.051</i>	50-1000 nm 0.015 0.044	Colloids sampled at the top and bottom of the column. High flow rate of 10 mL min <sup>-1</sup> means complete column porewater replacement approximately every 36 hours. Data based on colloid populations and
	Sample 2 (week 4) average Sample 3 (week 12) average	$\begin{array}{c} 1.2 \times 10^{13} \\ 5.0 \times 10^{13} \\ 1.6 \times 10^{13} \\ 6.5 \times 10^{13} \end{array}$	$4.4 \times 10^9$ $5.5 \times 10^9$ $2.4 \times 10^9$ $2.2 \times 10^9$	0.032 0.019 0.022 0.006	0.030 0.017 0.021 0.005	mass distribution. NB Background colloid mass in stock leachate of 0.002 mg dm <sup>-3</sup> (very close to analytical limit)

Study	Methodology	Colloid Population (dm <sup>-3</sup> )	Colloid Concentration (mg dm <sup>-3</sup> )	Comments
BGS microcosm experiments [99,100,101]	Incubation cells containing simulated waste, containment and backfill materials in synthetic groundwater. S/L = 1:330	average 5 × 10 <sup>9</sup>	-	Constantly stirred system. Colloid populations collected on 15 nm pore size ultrafiltration membrane.
Nirex combined waste ELTs [23,30,31]	Two 30 dm <sup>3</sup> -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.	< 2 × 10 <sup>9</sup>	-	Estimated upper limit for 0.1-5.0 µm size fraction in equilibrium leachates after 3 months storage following completion of the tests (based on low resolution SEM).
	ELT1 S/L ratio = ~1:1 at start Solids 53% NRVB, 36% grout by weight	$\begin{array}{cc} \text{ELT1} & 8\times10^8 \\ \text{ELT2} & 4\times10^8 \end{array}$		Measured populations for 0.1-5.0 µm size fraction in equilibrium leachate after 15 months storage
	ELT2 S/L ratio = ~1:2 at start Solids ~8% NRVB, 69% grout by weight	<10 <sup>10</sup>		Estimated upper limit for 0.1-5.0 µm size fraction in equilibrium leachates at the end of tests based on recovery of deposited material from containers after 15 months storage
Maqarin natural analogue study [14]	Collection of groundwater at the cement/host rock interface	1.15-4.89 × 10 <sup>10</sup>	0.051-0.190	Cement leachate travels through fractures in the cement, so data representative of fractured EBS (and may include erosion-derived colloids).

Notes:

ELT = Equilibrium leach testS/L = solid to liquid ratio



#### b) Nirex batch leaching experiments

In work for Nirex, initial studies of colloid generation were undertaken on granules of crushed NRVB and grout materials 3:1 PFA:OPC and 3:1 BFS:OPC [27]. NRVB was leached in demineralised water; the grouts were leached in both an NRVB-equilibrated water and a simulated Sellafield (saline) water equilibrated with NRVB. Leachates were prepared at three solid to liquid ratios (1:5, 1:10 and 1:50), up to three temperatures (room temperature, 60°C and 80°C) and for durations ranging from one week to five months. Prior to sampling, the high-temperature leaching experiments were immersed in cold running water to accelerate cooling. Leachate samples were examined by transmission electron microscopy (TEM) and photon correlation spectroscopy (PCS).

Subsequent work on the Nirex programme focused on leaching of NRVB, first of granules and later of rectangular monoliths that were cut from sticks of cured NRVB; all experiments were undertaken at ambient temperature. In most of the experiments, leaching was undertaken in demineralised water, although some early experiments were undertaken in Volvic water and a simulated saline groundwater.

Solid to liquid ratios (S/Ls) of 1:50, 1:10 and 1:5 were used in experiments with granules and values of about 1:42, 1:10 and 1:5.2 (with respect to dry cement weight) were used for the monolith experiments. S/Ls in the latter progressively increased as leachate volumes removed on sampling were not replaced with fresh solution. Leaching times for the experiments with granules varied from 36-41 days. Monolith experiments were sampled after 36 days and then at about six-monthly intervals up to 34 months. S/Ls on final sampling were estimated to be: 1:23.9, 1:6.5 (both 947 days) and 1:1.7 (1034 days) respectively. Most of the colloid analysis was undertaken by TEM, using methods described below. However, there was significant interference with quantification of the colloid populations due to the formation of very fine artefact particles (< 50 nm in size) during sample preparation that masked the smaller particle fractions of the NRVB colloid population. Therefore, towards the end of the monolith leaching study, SEM was preferred for colloid analysis with a significant improvement in controlling artefact formation.

#### NRVB granules

In contrast to the early UKAEA studies, an objective of studies of colloid formation undertaken on the Nirex programme was to quantify colloid populations generated from cementitious repository materials. Following development of an appropriate methodology for colloid analysis by TEM, a range of batch leaching experiments were undertaken on granules of crushed NRVB from different material batches, in demineralised water at three solid to liquid ratios (1:5, 1:10 and 1:50) [19]. Leaching times were typically 34-41 days before analysis of undisturbed leachate by TEM. Several types of colloidal-sized particles were identified: Mg- and Alcontaining, hydrotalcite-like flakes, Ca-, Al- and S-containing, ettringite-like rods and spheroidal Ca- and Si-containing CSH particles. In terms of particle numbers, ettringite flakes and CSH particles predominated, with the CSH particles dominating in terms of mass and volume. Particles varied in size between about 20 nm to over 500 nm in length with no predominant modal sizes for the limited numbers of particles counted. Total number concentrations were estimated to be about  $4 \times 10^{10}$  dm<sup>-3</sup> (Table 2.3) based on counting higher resolution images, although a bias towards regions of higher coverage for imaging purposes was recognised. Thus the results should be regarded as semi-guantitative and and are considered to overestimate the colloid populations in each case. From a qualitative viewpoint, observation of images at lower magnification suggested that particle coverages were roughly in proportion to the solid content of the experiments. These results were interpreted as providing a strong indication that the observed colloid populations resulted primarily from the dispersion of colloids generated from the NRVB by crushing.



Table 2.3	Results of colloid characterisation for of leachates of granulated NRVB (mix
	no. 95/009) in demineralised water at ambient temperature after 41 days [19]

Solid:liquid ratio	Mean r di	number dens spersion ≥ 1 (particle	sity of parti  5 nm in siz s dm <sup>-3</sup> )	Distribution by particle type (%)			
	Total	Spheroids	Rods	Flakes	Spheroids	Rods	Flakes
1:5	$4.6  imes 10^{10}$	$2.0\times10^{10}$	$2.2 \times 10^{10}$	$4.4  imes 10^9$	45	45	10
1:10	$4.3\times10^{10}$	$2.4\times10^{10}$	$1.6 \times 10^{10}$	$2.6  imes 10^9$	56	38	6
1:50	$4.1\times10^{10}$	$1.3  imes 10^{10}$	$\textbf{2.4}\times\textbf{10}^{10}$	$4.4  imes 10^9$	33	58	10

Given that crushing is not a process that will arise in a cementitious repository, it was considered that the results obtained on leaching crushed material would not be representative of colloid populations generated in the repository near field. On the other hand, the types of colloids observed may be representative of the types of particles that may be released from the backfill due to spalling from the surfaces of cracks, etc that are expected to form in the NRVB in a repository.

#### NRVB Monoliths

In view of the results described above, further leaching experiments with NRVB focused on leaching of monolith samples. Duplicate series of leaching experiments were undertaken in demineralised water. Aliquots of one set of leachates (A series) were sampled after 36 and 180 days leaching and colloid populations examined by TEM. The second set of experiments (B series) was sampled after 12 and 18 months. Over this time, the colloid concentrations measured in undisturbed leachates appeared to be very low and possibly less than ~10<sup>10</sup> particles dm<sup>-3</sup>. However, owing to the formation of artefacts on the TEM grids (at coverages that would be equivalent to leachate colloid concentrations of ~10<sup>11</sup> particles dm<sup>-3</sup>) and the low number concentrations, the leachate colloid populations were not well characterised<sup>4</sup>. Further analysis campaigns were undertaken by SEM with the collection of colloids from larger leachate volumes so that NRVB-derived colloid populations were unambiguously isolated. The three B-series experiments were re-examined after 24 and 31 months' leaching, and in one case after 34 months.

Colloid concentrations measured after 24 months leaching were in the range 10<sup>10</sup>-10<sup>11</sup> particles dm<sup>-3</sup>, somewhat higher than was estimated after 18 months. A variety of colloid types were identified including Ca-rich (calcium carbonate), CSH, Mg-Al (hydrotalcite-like) and rod-like Ca-Al-S (ettringite-like) particles, that are typical of NRVB leachates. Similar particle types were identified on TEM grids prepared after 31 months (937 or 944 days) leaching. The colloid size distributions show a typical power law relationship between number concentration and particle size (as per equation 2.2); the number concentration is dominated by

<sup>&</sup>lt;sup>4</sup> The exception to this was after 180 days leaching when, misleadingly, the A-series leachates were found to contain clusters of Ca-P-Si particles (as reported in [19]). However, these particles were found to be absent from the B-series leachates sampled after one year [28]. Further investigations confirmed that these particles arose accidentally due to contamination of the A-series experiments with phosphate buffer during pH measurements (undertaken *in situ* due to an error in following protocol) [29].

the smallest-sized (<100 nm size) components of the distribution while the mass concentration is dominated by the largest (>1000 nm).

On sampling for SEM (by decanting) after 31 months leaching, the presence of a fine, free-flowing sediment was observed in the bottom of each experiment. The amount of sediment appeared to be proportional to the (initial) solid to liquid ratio. SEM filters prepared from the highest solid to liquid ratio sample (M1B) at this time showed high particle coverages due to the presence of micron-sized particulate material. Nevertheless, the estimated colloid concentrations were of a similar order to those measured after 24 months, i.e. 10<sup>10</sup>-10<sup>11</sup> particles dm<sup>-3</sup>. However, the particulate and colloidal material was predominantly Ca-rich (calcium carbonate); the rod-like Ca-Al-S (ettringite-like) particles that were abundant after 24 months were no longer present. It appears that the colloid population had been disturbed by the re-suspension of the sediments and that the ettringite-like particles may have been removed by aggregation or forced sedimentation with fast-settling particulate material. After standing undisturbed for 3 months, experiment M1B was re-sampled. The particulate material had sedimented from the leachate and the colloid concentration was very low and <10<sup>10</sup> particles dm<sup>-3</sup>.

On termination of the experiments after 39 months, the leachate compositions were similar regardless of solid to liquid ratio and typical of NRVB-equilibrated water. However, relatively high carbonate concentrations were measured in each case (up to 400 ppm) due, it is thought, to the re-suspension of sediments during sampling.

The fine sediment appeared to arise primarily from the limestone flour component of the NRVB. It is possible that some of this material comprises residual NRVB fines arising from monolith cutting that may have been present from the start of the leaching experiments. However, the concentration of colloidal material arising from residual cutting fines appears to be very low (<10<sup>10</sup> particles dm<sup>-3</sup>). The principal mechanism of particle release from the NRVB monoliths during the experiments is considered to be spallation due to ongoing dissolution of the monolith surfaces. Some particle release may also occur due to grinding between the monoliths when the experiments are handled. Sub-micron particles such as CSH, ettringite-like and hydrotalcite-like phases may be released as colloids while larger particles (in particular limestone flour) sediment.

#### Grout granule leaching

In early studies of colloid generation from cementitious materials undertaken on the Nirex programme, reported in [27], leaching experiments were carried out on granules of 3:1 PFA/OPC in NRVB-equilibrated water and a simulated saline NRVB-equilibrated water at solid to liquid ratios of 1:5 and 1:50. Colloid populations in ambient leachates after one week were measured to lie between  $10^{10}$  and  $2 \times 10^{11}$  particles dm<sup>-3</sup> based on TEM analysis. The particles, some 300-500 nm in size, were composed principally of silica and appeared to be agglomerates of smaller particles. No colloids were detectable in the ambient temperature leachates by PCS but, based on the limit of detection, an upper limit of  $2 \times 10^{11}$  dm<sup>-3</sup> was estimated for the colloid population. Given that leaching was performed on crushed material, it is likely that the observed colloid populations arose predominantly from the redispersion of colloids generated by crushing.

PCS studies on 3:1 PFA:OPC leachates prepared at elevated temperatures and subsequently cooled to room temperature for analysis showed the formation of colloid populations as a result of nucleation and growth processes on cooling (see Appendix A in [19]). While these observations demonstrated the occurrence of colloid nucleation and growth processes from supersaturated cementitious leachates, and may indicate a potential method for preparing cementitious colloids for use in other experiments, such a rapid change in temperature is far from representative of repository conditions.

The results of parallel experiments to study colloid release from crushed 3:1 BFS/OPC are reported in [27]. However, later studies [19] confirmed that the colloid populations observed on



TEM grids were dominated by Ca-rich artefact particles that were not representative of the true colloid populations, which as a result had been overestimated. Considering also that the study was undertaken on crushed material, the results are not considered to be useful and so have not been included here. Difficulties were also encountered in characterising colloid populations from BFS/OPC grout leachates by TEM in work for CRIEPI, as outlined below.

#### c) CRIEPI batch leaching experiments

Experiments were undertaken on two cementitious materials under consideration in the Japanese programme, a low alkaline pH backfill material, High Flyash and Silica fume-content cement (HFSC), and a high pH, grout 9:1 BFS/OPC [98]. Leaching was undertaken using a synthetic groundwater, the Japanese fresh-reducing-high pH groundwater. Less than 250  $\mu$ m-sized fractions of crushed cement samples were leached at solid to liquid ratios of 1:5, 1:50 and 1:100 at ambient temperature at 60°C. The experiments were leached under essentially static conditions without significant disturbance and were sampled after leaching times of 2 and 8 months. Colloid populations were analysed by TEM using methods described below.

#### Crushed HFSC leaching

The results of colloid analysis of leach tests undertaken by AEAT and CRIEPI on High Flyash and Silica fume-content cement (HFSC) by TEM are summarised in Table 2.4 for experiments at room temperature [98]. Very similar results were obtained at 60°C. As observed on the TEM grids, the particles were apparently aggregated into small groups and clusters. For the purpose of analysis it was assumed that the particles were not aggregated in the leachate. Therefore, distinguishable particles were counted individually and the resulting particle number concentrations may represent upper limits for the leachate populations. The analysis covered a size range from 15 nm up to  $1.2 \,\mu$ m.

### Table 2.4 Summary of the results from TEM observation on colloids generated from HFSC leaching experiments at room temperature (from [98])

Leaching	Solid to	Colloid conc	Shape and composition	Colloid size distribution	
time	Liquid ratio	(dm <sup>-3</sup> )	of the colloids	Range (nm)	mean size (nm)
	1:5	<1 × 10 <sup>11</sup> (*)	D: Spheroidal (Si, Al, Ca)	Relatively coarse, widely distributed	N.D.
2 months	1:50	1 × 10 <sup>12</sup>	D: Spheroidal (Si, Al, Ca) M: Rod-like (Al, Si), Plate-like(Ca)	10-500	68
	1:100	$4 \times 10^{11}$	D: Spheroidal (Si, Al, Ca) M: Rod-like (Al, Si), Flake-like	10-500	76
	1:5	6.3 × 10 <sup>10</sup> (*)	D: Spheroidal (Si, Al, Ca) M: Spheroidal (Ca)	Relatively coarse, widely distributed	200
8 months	1:50	$1.1 \times 10^{12}$	D: Speroidal, (Si, Ca, Al) M: Rod-like, Plate-like	10-250	66
	1:100	1.1 × 10 <sup>12</sup>	D: Spheroidal (Si, Al, Ca) M: Flake-like	10-250	68

D: dominant particles, M: minor particles, (\*): artefact generated, N.D. not determined.

The results obtained at room temperature and  $60^{\circ}$ C showed similar trends with S/L ratio. The colloid concentrations of leachates with the lower S/L ratio (1:50 and 1:100) were found to be in the range of  $10^{11}$ - $10^{12}$  particles per litre. The majority of these particles were composed



predominantly of Si, Ca, and Al and were spheroidal in shape; the mean particle size was less than 100nm. Lower colloid concentrations were found in the leachates with the highest S/L ratios (1:5), which were  $\leq 10^{11}$  particles per litre. These leachates contained broader ranges of particle size with no clear modal size. For each S/L ratio, there appeared to be no major changes in the colloid population, composition and shape, particle size distribution or mean particle size in the leachates from 2 to 8 months. In addition, no significant change in colloid population with time over 36 days following separation from the solid phase was observed for one low S/L ratio (1:100) leachate.

The composition of the predominant particles was equivalent to the bulk composition of HFSC; the broad distributions of particle size were considered to be consistent with particle generation either by spalling from the cement during leaching or disintegration of the cement to produce colloidal-sized particles on grinding followed by dispersion on leaching.

The variations in colloid populations with S/L were correlated with the calcium concentration of the solutions controlling particle stability. See Section 3 for further discussion.

#### Crushed 9:1 BFS/OPC leaching

Attempts to study the colloid populations in leachates of 9:1 BFS:OPC grout by TEM using similar methods were less successful, however, owing to the tendency for artefact particle and deposit formation during the preparation of the TEM grids. Very small Ca- and Si-containing particles less than 10nm in size were found consistently on both leachate grids and ultrafiltered solution blanks. This effectively masked the colloid populations deposited from the leachates. No distinctive population of characteristic, larger BFS/OPC particles could be unambiguously identified on the grids on top of the artefact background suggesting that colloid concentrations in the size range 15 nm to 1.2  $\mu$ m were in fact very low. This view requires verification by other techniques.

#### d) PSI Batch leaching experiments

PSI [9] have used batch methods, to examine the stability of near-field colloidal dispersions arising from the Nagra M1 backfill mortar and quartz aggregate material, but the methodology was rather different from the static leaching experiments outlined above. Crushed material was added to young cement leachate (i.e. Na/KOH at pH 13.3) in a regime which was said to represent the stagnant conditions expected in a cementitious near field. Leaching was undertaken at a solid to liquid ratio of 1:10 in 800 cm<sup>3</sup> volumes of leachate solution. In some cases, an 'alkali cement water (ACW)', representative of a calcium hydroxide pH-buffered system (about pH 12.5), was used; in another two, sodium isosaccharinate (Na-ISA) was added to ACW to assess the impact of cellulose degradation products.

The mixtures were turned end-over-end for 2 minutes twice a day to thoroughly mix the solutions. For sampling, the mix was agitated again and allowed to stand for 1 minute following agitation before a 5 cm<sup>3</sup> 'total colloid' sample was taken. Following a further 24 hour wait to allow sedimentation of particles >1000nm nominal diameter, a further 60 cm<sup>3</sup> sample was taken. The 65 cm<sup>3</sup> aliquot was replaced by fresh solution before re-starting the experiment.

The experiment was extended by increasing the 24 hour pause to a period of 150 - 200 days (following 180 - 330 days of end-over-end agitation as above).

Colloid populations were analysed using the single particle counting technique (see sub-section 2.2 for details).

No significant differences were observed in the resultant colloid populations for the mixtures of different leachates or solid phases (Table 2.2), but the populations did decrease by an order of magnitude between the subsequent handling stages. Thus the 'total colloid' populations (sampling 1 minute after agitation) were the highest, followed by the 'undisturbed colloid'



populations (sampling 24 hours after agitation) and the 'steady-state colloid' populations (sampling 150 – 200 days after agitation). Interestingly, the 'steady state' values were just above the background values measured in the evolved leachate before interaction with the solid phase [9] and, despite significant effort by the experimenters, it proved impossible to lower these values.

Although this experiment was said to represent the stagnant conditions of a cementitious near field, it is clearly not the case. First, this is a relatively simple representation of repository conditions, even when compared to the simplistic ELT experiments, below. Second, the solid:liquid ratio is of little relevance, third, the timescales are too short for any meaningful interpretation and, fourth, it is clear that the agitation of the system made a difference. Even if the higher colloid populations were seen to decrease relatively rapidly when true stagnation was allowed to set in with the steady-state experiments, it would be interesting to see how such a system would further evolve over longer timescales (i.e. years to decades).

However, with the current set-up, the high background colloid populations in the stock leachate could make any more detailed interpretation impossible. According to [9], it was impossible to significantly reduce this background, despite the investment of significant effort, so this would have to be viewed as the method detection limit. If more appropriate, longer-term experiments are to be considered, then this is clearly an area to be tackled.

#### e) PSI column experiments



#### Figure 2.6 Experimental set-up of the COLEX I column [96]



Full details of the experimental set-up are given in [9] but, briefly, the experiment was carried out in a 2.69 m long (total volume 158.8 L) column (Figure 2.6) filled with M1 mortar with a porosity of 27% and a permeability of 10<sup>-10</sup> m<sup>2</sup>. The cement leachate was representative of a calcium hydroxide-buffered leachate and flowed through the column at 10 ml min<sup>-1</sup> (i.e. complete column porewater replacement every 72 hours or so). Previous experiments on the column as part of COLEX I means that it is likely that the M1 backfill had also degraded to Stage II cement by the time colloid samples were collected [9] and, indeed, the waters sampled from the column showed portlandite buffering, as would be expected if this were the case.

The pre-conditioning of the column due to the previous experiments means that it is likely that the cement-leachate system was in equilibrium (i.e. buffered to pH 12.5 by  $Ca(OH)_2$ ) during the period of colloid sampling. Leachate samples were taken from the top and bottom of the column and colloid concentrations were determined by single particle counting in the leachate itself (using methods described in sub-section 2.2.4).

#### Results

The measured colloid populations (Table 2.2) in leachate samples from near the top and bottom of the column were in the range  $10^9$  to  $2 \times 10^{10}$  dm<sup>-3</sup> for the 50-1000 nm size range. To estimate the concentration of particles of smaller size (1-50 nm), the particle size distribution was plotted as a log-log plot, fitted with a power law (equation 2.2) and the data extrapolated to 1 nm. The resulting colloid populations for the 1-1000 nm size range have also been included in Table 2.2. The extrapolated populations are 3 to 4 orders of magnitude higher than the measured populations. This suggests that there may be significant colloid populations in the 1-50 nm size range. However, the authors recognised that: "...the measurements...provide no unequivocal evidence whether or not an extrapolation of the size distribution to the lower end of the colloidal size spectrum [based on power-law scaling] is fully justified". Thus the estimated concentrations for the 1-1000 nm size considered to be cautious.

Colloid masses were estimated from the particle size distribution assuming that the particles were uniform spheres.

In the measured size range, the colloid number concentrations decreased by up to an order of magnitude between week 1 and week 12 samples. Initially more colloids were found in the bottom leachate for all size classes, but the results were similar after 12 weeks. In general, the measured colloid populations were similar to those measured in the batch leaching experiments after 24 hours standing, although comparison between the results is limited due to differences in the water chemistry in the two sets of experiments.

While the integration of near-field colloid analysis in COLEX I is to be applauded, it is questionable whether such column experiments are worth repeating. The erosional effects of the relatively fast moving leachates through a crushed (rather than intact) mortar are not representative of stagnant conditions in a geological cementitious repository. It is unclear whether the experimental set-up may be more representative of surface or near-surface facilities.

#### 2.3.2 Equilibrium leach tests

#### a) BGS microcosm experiments

In the BGS experiments, after an initial lengthy period of equilibration, the cell solution pH remained relatively stable at 11.5–12 and the Eh around -100 mV. The cells were stirred continuously and supernatant solution was removed (from the upper third of the cell) by syringe and colloids collected by sequential, cross-flow membrane ultrafiltration (15–1000 nm) from a 2 cm<sup>3</sup> sub-sample.



The relevance of the early ELT experiment of BGS [99,100,101] to near-field colloids is questionable as, obviously, the mixture of materials is rather idealised and the proportions are nowhere near those of a cementitious repository. Here (Table 2.2), the S/L ratio of approximately 1:330 is extremely unrealistic, but was presumably necessary to provide enough sample volume for the range of analyses (leachate chemistry, microbial populations, colloid populations etc) carried out. Under realistic conditions, the leachates would be massively dominated by cementitious materials of the EBS which would produce alkaline conditions (> pH 13 at first) and this and the high Ca concentrations in the leachate would act to minimise colloid populations. In cell 3, the focus of the colloid studies, initial pH was around 9 and slowly rose to a peak of 12 at 300 days and the initial Ca concentration of 35 mg dm<sup>-3</sup> slowly rose to a peak of 130 mg dm<sup>-3</sup> around 280 days before dropping to 80 mg dm<sup>-3</sup> by day 550. This strongly suggests that the measured colloid populations are likely to be much higher than repository *in situ*.

In addition, the constant stirring of the solution is also likely to maximise colloid populations by erosion etc. Finally, the colloid chemistry was almost certainly affected by the experimental setup, with periods of oxygenation of the cells following seal failure. This can be seen in the fact that 100% of the Fe in solution is removed on a 15 nm nominal pore size filter, suggesting colloidal Fe oxyhydroxides are present in the cell.

#### b) Nirex equilibrium leach tests

In the AEAT experiments, two ELTs (ELT1 and ELT2) using representative proportions of real ILW, encapsulation grouts and NRVB were carried out on the 30 dm<sup>3</sup> scale. The two tests differed in that ELT2 contained essentially no NRVB. The overall NRVB, encapsulation cement and waste contents of the two equilibrium leach tests are summarised below:

ILW wastes:	2.305 kg
Cured encapsulation matrices:	7.224 kg
Cured NRVB:	10.7 kg (ELT1) and 0.8 kg (ELT2)
Groundwater simulant (BH2 DET8)	20.3 dm <sup>3</sup> (at commencement)
Including entrained groundwater <sup>5</sup> :	8.95 dm <sup>3</sup> (ELT1) and 5.95 dm <sup>3</sup> (ELT2) (This meant that there were 11.35 dm <sup>-3</sup> and 14.35 dm <sup>-3</sup> of water above the original level of the wastes in ELT1 and ELT2 respectively).

<sup>&</sup>lt;sup>5</sup> Entrained groundwater refers to the volume of synthetic groundwater added to the tests to just cover the surface of the solids. It does not take account of any water incorporated as porewater in the matrices or in wet wastes.



Figure 2.7 Schematic view inside AEAT ELT containers (from [102])

Each test contained 17 different major ILW wastes expected to be present in the Nirex repository including a variety of metals (mild and stainless steel, aluminium, zircaloy), swarf and sludge derived from Magnox fuel decanning, flocs from precipitation process, anion exchange resins and a variety of polymeric and cellulosic materials. The tests were put together in a layered structure of alternate nominally cement and waste layers with portions of groundwater simulant. The top layer contained only NRVB and/or cement grouts. Each test was heated by means of an immersion-heater separated from the waste/ cement mix within a vented stainless steel tube. The two ELTs completed six years of operation at 50°C, with regular sampling of the leachate, in July 1998. They then ran for another nine months at ambient temperature. Measurements at the end of the tests indicated that the conditions were not reducing; final pH values were 12.5 for ELT1 and 12.2 for ELT2. Full descriptions of the tests, their commissioning and periodic sampling results are given in [102]. Schematic cross-sections of the experiments during operation are shown in Figure 2.7.

An initial SEM study of the colloid populations in ELT leachate and redispersed fines samples was undertaken as part of the decommissioning of the tests [30]. However, owing to the radioactivity of the specimens, they were studied using a low resolution SEM and the particles were difficult to resolve and identify. A further study was made 15 months after leachate collection using a higher resolution SEM instrument [31], that allowed colloid particles down to about 30 nm in size to be studied. Three leachate samples taken from each test were examined. These were:

- the bulk supernatant leachate that was collected from above the solid wastes at the end of the test, referred to as the equilibrium leachate (designated ELT1/A and ELT2/A);
- the decanted supernatant leachate from a fines sample that was obtained by agitating leachate across the top-surface of the solid to collect any suspendable solids (designated ELT1/V and ELT2/V);
- the decanted supernatant leachate from a fines sample obtained by agitating and draining leachate in the heater-tube well in the waste (designated ELT1/H and ELT2/H).

Specimens for SEM analysis were prepared by collecting particles from known volumes of each sample (pre-filtered through a 5.0 µm filter) onto a 0.1 µm pore-sized track-etched membrane filter. Each filter was then washed with pH 11.5 NaOH solution to remove residual solutes before drying. A set of filters was first prepared for  $\alpha$ -,  $\beta$ - and  $\gamma$ -activity analysis, the activity results being used to select appropriate sample volumes for the SEM filters.

To investigate whether a significant amount of colloidal material had been lost from the leachates by sorption to the bottle walls or sedimented during 15 months storage, the bottles were washed with pH 11.5 NaOH solution and ultrasonicated to redisperse deposited material. The wash solutions were used to prepare a second set of filter specimens for activity and SEM analysis.

#### Results

Initial colloid analysis of leachate and fines samples from the two Nirex ELTs was hampered by the poor resolution of the SEM instrument used and difficulties in distinguishing colloidal particles from artefacts in the images collected. An estimated upper limit for colloid populations in the equilibrium leachates for the 0.1-5.0 µm size range was  $\leq 2 \times 10^9$  dm<sup>-3</sup> [30]. The results of the later study are summarised in Table 2.5 [23,31]. In this sub-section the colloid population data will be discussed; the associated activities will be considered in Section 4.

The particle concentrations in 0.1-5.0  $\mu$ m filtered fractions of the equilibrium leachate after storage for 15 months, were confirmed to be very low at 8 × 10<sup>8</sup> dm<sup>-3</sup> and 4 × 10<sup>8</sup> dm<sup>-3</sup> for ELT1 and ELT2, respectively. Ultrasonic, alkaline washing of the storage bottles after sampling showed that a significant amount of the colloidal phase was lost by attachment to the bottle walls or by sedimentation during storage. Based on the colloid recovery from the storage bottles in a single washing step (which cannot be assumed to be fully quantitative), the particle number concentrations for the 0.1-5.0  $\mu$ m size fraction in the two equilibrium leachates at the end of the tests were estimated to be about 10<sup>10</sup> dm<sup>-3</sup>.

The particles are predominantly roughly spheroidal particles of calcium carbonate, varying in size from about 50 nm to 1  $\mu$ m. The ELT1 equilibrium leachate also contained a distinct population of rod-like particles, 1.0-1.5  $\mu$ m in length and 240-500 nm in width, with a similar composition at a concentration of about  $6 \times 10^7$  dm<sup>-3</sup>. There was also evidence for bacterial populations in both tests, and a concentration of  $3 \times 10^7$  organisms dm<sup>-3</sup> is estimated in the stored supernatant leachate from ELT2.

Decanted supernates from three of the four fines samples studied contained very low colloid concentrations after 15 months storage (<10<sup>10</sup> dm<sup>-3</sup>). Although, a significant amount of colloid material was recovered by ultrasonic washing from the bottles used to store the heater-well fines supernates from each test, the total colloid concentrations in both ELT1/H and ELT2/H, including recovered material, were estimated to be below 10<sup>11</sup> dm<sup>-3</sup>. These populations were also composed predominantly of roughly spherical calcium carbonate particles, but a wider variety of particle types were identified than in the equilibrium leachate liquors, particularly in ELT2/H. These included iron/chromium oxide particles in ELT1 arising from steel corrosion, whereas in ELT2 iron appeared to be incorporated predominantly into mixed oxide phases, in particular, into a population of spherical Ca-Si-Al-Fe particles, 200-500 nm in size.



A significant amount of colloidal material was dispersed from a gel layer on the top surface of ELT2 by agitation of leachate at the end of the test. This material appeared to form a stable colloidal dispersion and there was measurable alpha activity associated with the colloidal phase. The population consisted primarily of small brucite particles ~300 nm in size with a number concentration of at least  $3 \times 10^{11}$  dm<sup>-3</sup>. There was also a distinct population of spherical Ca-Si-Al-Fe particles with a concentration of about  $10^9$  dm<sup>-3</sup>. The latter type of particle was also found in the equilibrium leachate whereas brucite was not.

Table 2.5 Summary of particle types, concentrations and associated activities for particle fractions (< 5 µm to >0.1 µm) isolated from ELT leachates and sample bottle wash solutions after 15 months storage at ambient temperature; also included are measured leachate activities (after 0.45 µm filtration) at the end of the ELTs

Sample Number concentration		Activ (Bq d	∕ities dm <sup>-3</sup> )	Major Particle Types <sup>‡</sup>	
	(particles dm <sup>-</sup> ) '	α	β		
0.45 µm-filtere					
ELT1	-	3.3 <sup>§</sup>	$2.2 \times 10^{7  \#}$	-	
ELT2	-	2.2 <sup>§</sup>	$2.1  imes 10^{7  \#}$	-	
Leachates					
ELT1/A	$8.4\pm0.9\times10^8$	<0.35	$2.5  imes 10^4$	CaCO <sub>3</sub>	
ELT1/H	$2.4\pm0.6\times10^8$	<10	$2.4  imes 10^4$	CaCO <sub>3</sub>	
ELT1/V	$8.0\pm0.9\times10^9$	110	$1.8 \times 10^{4}$	-	
ELT2/A	$4.0 \pm 0.4 \times 10^8$	<0.25	$2.5  imes 10^4$	CaCO <sub>3</sub>	
ELT2/H	$2.3\pm0.5\times10^9$	55	1.1 × 10 <sup>4</sup>	CaCO <sub>3</sub> , Brucite	
ELT2/V	*	$7.3 \times 10^{3}$	$7 \times 10^4$	Brucite, Ca/Si/Al/Fe	
Sample bottle	wash solutions				
ELT1/A/US	$4.3\pm0.6\times10^9$	5.5	$9.5 \times 10^{3}$	CaCO <sub>3</sub> , Ca/Si/Mg, Si/Mg	
ELT1/H/US	$7.0 \pm 1.5  imes 10^{10}$	1.8 × 10 <sup>3</sup>	2.4 × 10 <sup>5</sup>	CaCO <sub>3</sub> , Fe/Cr, CSH, Si/Al/(K,Na) (clay), Si/Mg	
ELT1/V/US	-	55	$8.5  imes 10^3$	-	
ELT2/A/US	$9.3 \pm 0.7  10^9$	60	5 × 10 <sup>4</sup>	CaCO <sub>3</sub> , Ca/Si/Al/Fe, Si/Mg, Si/Al/(K,Na) (clay), Brucite	
ELT2/H/US	$2.7 \pm 0.7 \ 10^{10}$	720	1.9 × 10 <sup>4</sup>	SiO <sub>2</sub> , Ca/Si/Al/Fe, Brucite, Si/Mg, Si/Al/(K,Na) (clay), Fe/Cr	
ELT2/V/US	-	$1.2 \times 10^{3}$	$4.6 \times 10^{3}$	-	

<sup>†</sup> Number concentration in the solution applied to the 0.1 µm Isopore filter.

<sup>‡</sup> Particle compositions based on major elements (oxygen, chlorine and trace elements omitted except where stated).

\* For top-surface fines sample ELT2/V, the number concentration could not be measured because the particle concentration on the filter was too high. The concentration of brucite particles appears to be  $\geq 3 \times 10^{11} \text{ dm}^{-3}$ .

§ Estimated from measured activities for <sup>241</sup>Am and <sup>239/240</sup>Pu [30].
 # Estimated from measured activities for <sup>90</sup>Sr (allowing for <sup>90</sup>Y daughter) and <sup>137</sup>Cs [30].

#### 2.4 Natural analogue studies

Currently, only one natural analogue study (see Box 2.1) of colloids in a cementitious aquifer has been studied – at Maqarin in Jordan [14]. Work is currently in progress at a new site at Mangatarem in the Philippines [118], an analogue for a low-alkali cement environment, although studies are concentrating on the interactions between low alkali cement leachates and bentonite<sup>6</sup>.

At Maqarin [14], the colloids were collected at the face of a tunnel (see Figure 2.8) from a fracture at the interface of the natural cement and the host rock. The major problem during sampling of the alkaline groundwaters is potential contamination from atmospheric  $CO_2$ . As noted by [119], the ingress of  $CO_2$  causes an immediate drop in the solution pH and the precipitation of a mixed carbonate/portlandite phase (seen clearly on the tunnel walls in Figure 2.8). Indeed, this was the main problem during a preliminary sampling campaign where carbonate/portlandite colloids precipitated out in the groundwater sample during transit. Another problem can be seen in Figure 2.8: the sampling site is in a narrow, dirty tunnel and dust, water dripping from the roof etc. are also potential contaminants. Both the above problems can be minimised by using a closed system for groundwater sampling (see Figure 2.3).

#### Box 2.1 What is a natural analogue?

There are many different definitions of 'natural analogues' in the context of radioactive waste disposal. A very general example is:

"...an occurrence of materials or processes which resemble those expected in a proposed geological waste repository." [1]

In this case, the occurrence is accepted to be either completely natural or anthropogenic, thus including archaeological analogues. In technical applications of natural analogues - which focus very much on the testing or validation of models (conceptual, qualitative or quantitative) - such general definitions cause confusion as just about any study of the geological environment could be classified as some sort of analogue on the basis of the definition above. For such cases, more specific definitions have been proposed, for example:

"...the essence of a natural analogue is the aspect of testing of models, whether conceptual or mathematical, and not a particular attribute of the system itself." [2]

Natural analogues are recognised as a potentially valuable tool for supporting PA, and may be used as good illustrations of repository behaviour. Thus natural analogue evidence can build confidence in repository concepts by showing that a repository system is not unique and that there are natural precedents for geological disposal.

1. Côme, B., and N.A. Chapman (Eds.). 1986a. 1st Natural Analogue Working Group Meeting, Brussels, November 1985. CEC Nuclear Science and Technology Reports. EUR 10315. Luxembourg

2. McKinley, I.G. (1989), Applying natural analogues in predictive performance assessment (1): principles and requirements; (2): examples and discussions; in Risk analysis in nuclear waste management, pp.357-396, Klewer Academic Publ., Netherlands. See also <a href="http://www.natural-analogues.com">www.natural-analogues.com</a>

<sup>&</sup>lt;sup>6</sup> The current study is looking at the impact of low alkali cement leachates on the host rock and the bentonite buffer or backfill for those designs where bentonite will be considered part of the EBS. Although the leachate source is not a natural cement, rather an ophiolite, the colloids produced are directly analogous to cementitious NF colloids as they are produced due to oversaturations in alkaline groundwaters with a chemistry very similar to low alkali cement leachates [118].



# Figure 2.8 Two views of the M1 sampling site, adit A-6, Maqarin, Jordan. The thick white precipitate on the tunnel wall is an intimate mixture of portlandite and carbonate (from [14]); the sampling equipment can be clearly seen on the tunnel floor

After clearing the tunnel wall of secondary precipitates, the rock face was examined to identify the areas of water flow. A Teflon<sup>®</sup> funnel was clamped directly to the wall over the main water conducting feature (see Figure 2.9) to aid collection and minimise contamination (after [120]). A Teflon<sup>®</sup> tube was attached to the funnel and the groundwater was allowed to flow by gravity (approximate flow rate of 100–200 cm<sup>3</sup> min<sup>-1</sup>) to the sampling cell, first being passed through a 1µm nominal pore size pre-filter (to remove any large particles dislodged from the fracture). The cell was connected to the inflow line and to a gas supply by a Teflon<sup>®</sup> three-way valve (Figure 2.3).

When the cell was overflowing, the valve was switched to the gas line and high purity ('White Spot')  $N_2$  at a maximum pressure of 3 bar was used to pass the water through the filter at the bottom of the cell. This was repeated three times per filter and only on the final volume was the cell fully emptied (i.e. dry filter). It was hoped that the rapid processing of several small volumes of the alkaline groundwater, rather than one larger volume, would also minimise colloid production due to  $CO_2$  uptake from the atmosphere. The first 20 cm<sup>3</sup> of filtrate was discarded for each filter to minimise filtrate contamination from the filter [51]. Upon removal from the sampling cell, the filters were immediately placed in plastic petri dishes which were sealed with shrink plastic, placed in sealed polythene bags and stored in sealed packing cases.

Obviously, the filter handling stage was the most crucial with respect to contamination and the utmost care was taken to avoid dust, water drips etc. touching the filters, petri dishes etc. but it is clear that, without laminar flow hoods or glove bags, it is impossible to guarantee absolute cleanliness (see Figure 2.8) so the data should be considered with caution.





Figure 2.9 M1 sampling site. Extensive secondary deposits, up to 30 cm thick, completely coat the walls of the Adit and had to be removed to fit the funnel to the rock (from [14])

#### 2.4.1 Results

Colloid concentrations measured at Maqarin were in the range 1.15 to  $4.89 \times 10^{10}$  dm<sup>-3</sup> which are comparable with colloid concentrations measured in leaching experiments with cementitious materials.

The conditions at the Maqarin site potentially differ from those in a deep repository in a number of ways:

- the sampling site is near-surface in a relatively high permeability zone;
- cement leachate (i.e. groundwater) flows through fractures in the (natural) cement (Figure 2.10), not through the cement matrix (which, in fact, is highly impermeable [121]);
- the cement leachate is semi-oxic to anoxic, depending on seasonal flow, etc.

In other words, the Maqarin natural analogue colloid data are representative of a near-surface repository that has suffered fracturing as the cement has aged and could be taken to represent an extreme case for a deep cementitious geological repository.



Figure 2.10 Flow at Maqarin is through fractures and joints in the cement mass (brown, top of photo) and from there into the host rock (black, bottom); here, the fractures have been sealed by secondary CSH (and locally zeolite) phases (note hammer on left for scale - from [121])

#### 2.5 ADZ-derived colloids

#### 2.5.1 ADZ in hard rock

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 (see Section 5.4). In a survey of laboratory experiments focused on host rock/cement leachate interactions [122], 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 [123] for details). Unfortunately, this was not included in HPF<sup>7</sup> but may be part of the ongoing LCS experiment at the same site (see <u>http://www.grimsel.com/lcs/lcs\_intro.htm</u> for details), so providing input in the foreseeable future.

<sup>&</sup>lt;sup>7</sup> An attempt was made to sample for colloids in the latter stages of the project, but it was thwarted by equipment failure.



Unfortunately, as with the laboratory experiments noted above, no other recent large-scale URL experiments, such as those at Mont Terri in Switzerland [124] or international collaboration projects [e.g. 125, 126] have focused on the issues of ADZ-derived colloids.

#### 2.5.2 Bentonite – alkaline plume interactions

As noted previously, although the current UK reference repository design for ILW does not include bentonite backfill, several others do, citing requirements for improved barrier function [e.g. 17] or for simplifying modelling the near-field source term ([e.g. 79] – cf. section above). As such, it is worth briefly reviewing the status of work on bentonite near-field colloids here.

Although much work has been carried out on the colloid barrier role of bentonite, little has been done to date on the aspect of the bentonite as a source of near-field colloids. Most work on colloid generation from bentonite [e.g. 127, 128] has focused on bentonite as a source of colloids in the geosphere due to erosion at the bentonite-host rock interface, a topic which is beyond the scope of this review.

Some work does exist on the alteration of bentonite in alkaline leachates [e.g. 129] and in low alkali cement leachates [e.g. 130] and the effect this has on colloid filtration by the bentonite, but only one reported study [131] has looked at the potential production of bentonite colloids during alkaline reaction. In that study, the authors reported the erosion of bentonite gels in NaCl solutions (0.01 to 0.5 mol dm<sup>-3</sup>) at pH 12 at flow rates of 6.4 to  $8.9 \, 10^{-5} \, \text{ms}^{-1}$  and in Ca(OH)<sub>2</sub> saturated solution at 2.1  $10^{-5} \, \text{ms}^{-1}$ . These values were somewhat higher than rates reported under far field conditions which estimated that the critical flow rate for erosion to occur and produce bentonite colloids is between  $2 \times 10^{-6} \, \text{ms}^{-1}$  (fresh water) and  $8 \, 10^{-6} \, \text{ms}^{-1}$  (seawater) [127]. Interestingly, in [131], erosion flow rates for bentonite gel in NaCl solutions (again, 0.01 to 0.5 mol dm<sup>-3</sup>) at pH 6 and 9 are higher still, at 2.1 to  $4.4 \times 10^{-4} \, \text{ms}^{-1}$ . Unfortunately, not enough information is presented on the methods employed to ascertain why the differences exist. Such eroded colloids could potentially be transported into the repository near-field or into the geosphere depending on location compared to the direction of groundwater flow. However, as noted in [131], it is likely that any eroded bentonite colloids will be unstable in the cementitious repository near field. Colloid stability is discussed further in Section 3.

#### 2.6 Organic-near-field colloid interactions

#### 2.6.1 Waste-derived organics

The focus of this section is on the interactions of soluble organic compounds arising in a repository either as-disposed or from degradation of organic waste materials with colloids, and the potential for such interactions to enhance colloid populations. The main sources of available information are a number of the experimental studies that have already been described including leaching experiments undertaken by PSI in the presence of ISA, the major product of the anaerobic degradation of cellulose, and the ELT experiments undertaken by BGS and AEA Technology which included organic waste components. Some characterisation of natural organics and their association with colloids was also undertaken at the Maqarin and Khushaym natural analogue sites in Jordan.

#### a) PSI leaching studies

In addition to the leaching of M1 backfill and quartz aggregate in cement-equilibrated water (ACW), PSI also undertook a number of experiments that included 5 10<sup>-3</sup> mol dm<sup>-3</sup> ISA to investigate whether its presence, at concentrations that potentially could arise in a repository would have any effect on colloid populations [9]. ISA is known to sorb strongly to cement phases in the alkaline cement water (pH 13.3) used in the tests [132]. About 16% of the added ISA was estimated to be sorbed to cement particle surfaces in experiments with M1 backfill.



The colloid concentrations measured after leaving the batch-type systems undisturbed for 24 hours after end-to-end mixing were slightly enhanced in the presence of ISA. In ISA-containing M1/ACW and quartz/ACW systems the concentrations were  $6.2 \pm 0.2 \times 10^{10}$  dm<sup>-3</sup> and  $1.4 \pm 0.2 \times 10^{10}$  dm<sup>-3</sup> respectively, compared to values in the range 1.5-8.5  $10^9$  dm<sup>-3</sup> for the ISA-free systems. In addition, the subsequent rate of colloid aggregation and sedimentation for the M1/ISA system over longer time scales was reduced, although no such retardation of aggregation was observed with the quartz/ISA system. Nevertheless, the resulting long-term colloid concentrations in the M1/ACW/ISA system remained very low at  $8.0 \pm 3.5 \times 10^8$  dm<sup>-3</sup>.

The above results indicate that although ISA sorption does exhibit a stabilising effect on M1 colloids at pH 13.3 in ACW (calcium concentration 1.6 10<sup>-3</sup> mol dm<sup>-3</sup>), the effect is too small to have a significant effect in the long-term. Therefore it was concluded that ISA would not have a significant adverse effect on the colloid inventory of a M1 backfilled near-field.

#### b) Equilibrium leach tests

Both the BGS microcosm experiments and the combined waste equilibrium leach tests combined the leaching of cements with simulated or real waste materials with significant organic content. However, in both sets of experiments the colloid populations measured in supernatant leachates were very low as indicated in Table 2.1. Thus there is no indication that the organic sorption-stabilisation mechanism has a significant effect on colloid populations over the two-and seven-year timescales, waste inventories and conditions of these sets of experiments.

#### 2.6.2 Organic cement additives

The interactions of organic cement additives, including superplasticisers, with cement phases that underlies their use in structural cements and concretes is a topic of research in the field of cement chemistry. However, such studies are not concerned with colloid populations but with understanding cement particle interactions that control the rheological properties of cement pastes. A number of examples are discussed in Section 3.6.

#### 2.6.3 Natural organics

#### a) Fulvic and humic acids

Natural organic materials (in particular humic-like and fulvic-like materials) are present, to some extent, in all natural waters including deep groundwaters and such materials may potentially migrate into a GDF with inflowing groundwater. In general, larger molecular weight humic acids are destabilized under the alkaline conditions of a cementitious near-field whereas lower molecular weight fulvic materials are more stable and may be mobile (see sub-section 3.4.3). Fulvic-like materials may potentially interact with colloids to increase their stability. The authors are not aware of any specific studies to investigate the potential effects of fulvic-like natural materials on near-field colloid populations.

#### b) Natural analogue studies

At the Maqarin and Khushaym Matruk natural analogue sites in Jordan, the host rock contains up to 15 wt% organic material [133]. Work was undertaken to study the dissolved organics in an attempt to assess their role, if any, in complexing radionuclides in the near field and ADZ; interactions with colloids were also considered. The dissolved organic material was found to be dominated (around 90%) by aliphatic compounds of a marine origin [134], presumably from the (marine) clay biomicrite host rock. The Dissolved Organic Carbon (DOC) was enriched in aromatics [134] and humic acids were found to be absent [135], suggesting that the majority of the DOC is, in fact, derived from locally leaching plant remains and thin soil horizons. Analysis of the near-field cement colloids collected at the Maqarin site produced no evidence of reaction with organics [14].



Interestingly, organic material appears to be deposited, along with secondary calcite, within the rock matrix in the ADZ at these sites. This suggests that there is an interaction of the natural dissolved organics with cementitious surfaces.

#### 2.7 Far-field natural colloids – a brief overview

Historically, far-field natural colloids have received much more attention than near-field colloids, but this is partly because of interest in their role in contaminant transport in shallow groundwaters [e.g. 136,137]. It is useful here to briefly examine the characteristics of far-field colloids of relevance to a geological repository, to help put the information presented elsewhere on near-field colloids in context.

It is worth noting that the sampling and characterization of natural colloid populations is not straightforward and that careful design and operation of sampling procedures and subsequent analysis is necessary to avoid the formation of unwanted artefacts that can lead to inaccurate results. After over 25 years of international experience, the issues and potential pitfalls of groundwater colloid sampling are recognized and well-documented and a variety of procedures have been developed to mitigate their effects. Nevertheless, care needs to be exercised in the interpretation of experimental data. There needs to be a good understanding of the groundwater chemistry and the aquifer mineralogy at the site and recognition of the potential perturbations of the system. In particular, drilling of boreholes induces significant changes to the rock-water system at depth, which can remain in disequilibrium for many years [e.g. 138,139]. Sampling deep waters may also perturb the water chemistry inducing artifacts, which are liable to increase colloid populations [e.g. 20]. Thus measured values are liable to be maximum values. In the context of a deep repository, such values will provide cautious estimates for far-field colloid populations.

It is beyond the scope of this report to discuss groundwater sampling issues and experimental procedures in detail, however, a number of reviews are available [e.g. 50,51,62].

Table 2.6 provides examples of natural colloid concentrations and compositions measured in groundwater sampling campaigns undertaken internationally. As noted in Section 1, apart from a few exceptions, far-field colloid compositions reflect the mineralogy of the water-conducting system in which they exist. As can be seen in Table 2.6, this tends to be simple mineral phases such as clays and quartz.

Reported colloid mass concentrations in deep groundwaters in crystalline rock vary widely between 0.0003 and 20 mg dm<sup>-3</sup>. In a number of cases, quoted concentrations are upper limits, reflecting uncertainties arising from water or sample perturbations during analysis. The highest reported concentrations in a deep groundwater (158 mg dm<sup>-3</sup>) come from the Gorleben site in Germany where the aquifer is rich in natural organic (humic) substances and the colloid population is predominantly organic.

Comparison of near-field colloid data in Table 2.2 with those in Table 2.6 indicates that colloid populations and concentrations measured under simulated near-field conditions are broadly similar to those measured in deep groundwaters.

Degueldre analysed relationships between colloid populations in granitic waters and local conditions. He noted that lower colloid concentrations could be observed at lower pH "...because aggregation is easier..." and that "higher concentrations are found in systems subject to change (hydrothermal activity, ionic strength or pH changes). The size distribution is then a function of pH and salt concentrations." He concluded that the most important parameter affecting measured colloid populations was the ionic strength of the groundwater and in particular the divalent metal ion (calcium and magnesium) concentration. The topic of colloid stability will be discussed in more detail in Section 3.



Site	Host rock	Groundwater	Colloid	Colloid	Colloid
		рн	(dm <sup>-3</sup> )	(mg dm <sup>-3</sup> )	composition
Whiteshell URL, Canada [140]	Granite	6.0	10 <sup>11</sup>	0.34	Silica, clay
Bad Säckingen, Germany [62]	Weathered granite	6.0		0.1	Quartz, clay
Gorleben, Germany [141]	Glacial sand and silt	7.8	5.3 10 <sup>17</sup>	158	Humic substances
Menzenschwand, Germany [62]	Granite	6.5		0.4	Clay
El Berrocal, Spain [142]	Granite	6.7	10 <sup>12</sup>	-	Silica, clays
Aspö URL, Sweden [68]	Crystalline	7.1 – 7.8		0.003 – 0.3	Calcite, quartz, clay, iron oxyhydroxides
Forsmark, Sweden [143]	Crystalline	7.2 – 8.3		0.001 – 0.2	Sulphur, iron oxyhydoxide*, illite
Leuggern, Switzerland [62	Granite	7.9		0.04	Quartz, clay
Zurzach, Switzerland [55]	Sediments/ top granite	8.0		0.02	Quartz, clay
Gas tunnel, Grimsel, Switzerland [55]	Granite	8.8		<2	Clay, quartz
Gas tunnel, Grimsel, Switzerland [55]	Granite	9.0		<1	Clay, quartz
Gas tunnel, Grimsel, Switzerland [55]	Granite	9.2		<20	Illite
Grimsel URL, Switzerland [144]	Granodiorite	9.6		0.0003 – 0.001	Quartz, illite
Wellenberg, Switzerland [145]	Metamorphose d marl	8.5		0.03	Clay
Sellafield, UK [146]	Sandstone	-	8 10 <sup>10</sup>	0.5	Silica coated with iron oxyhydroxides, illite

#### Table 2.6 Examples of natural far-field colloid concentrations and compositions

\* Presence of sulphur and iron oxyhydroxide are probably due to sampling artefacts.

#### 2.8 Current understanding of near-field colloid populations

Since the Nirex 97 assessment, a significant body of experimental work has been undertaken to characterise colloid generation from cementitious materials under simulated near-field conditions. The picture emerging consistently from these studies is that cementitious colloid concentrations under these conditions are low with number concentrations typically less than 10<sup>12</sup> particles dm<sup>-3</sup> for the size range larger than 15 nm, with maximum mass concentrations of less than 1 mg dm<sup>-3</sup>.

The formation of artefacts during specimen preparation from the cementitious waters in a number of the studies (particularly by TEM) has complicated the characterisation of the cement colloid populations; in these cases maximum concentrations have been reported. However, this has only served to emphasise that the true colloid concentrations are very low. The use of single particle counting techniques provides significant benefits in allowing water samples to be analysed directly without the need for intermediate specimen preparation, thus reducing the potential for artefact particle formation and lowering the limit of detection for colloid populations. It is not recommended that SPC should be used in isolation, however. Application of electron microscopy techniques and associated EDX analysis of particles is desirable to identify colloid types, morphologies and compositions.

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 [18]. 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 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.

It should be noted, however, that on the Nirex programme the smallest colloidal size fraction, nominally from about 1-3 nm in size, has been included as part of the dissolved phase, which has been defined by the use of 30,000 NMWCO filters for solid phase separation in both radionuclide solubility and sorption experiments. Thus the current data "gap" is effectively reduced.

Recent developments in analytical techniques, such as laser-induced breakdown detection (LIBD – see Appendix 1) potentially allow quantitative measurements of particles down to 1 nm size to be made. The technique has been used to study natural colloid populations in groundwaters [147] but has yet to be applied to near-field colloids.

Owing to the variety of experimental methods used, it is difficult to make direct comparisons between datasets for colloid generation from different materials. Crushing and cutting of cement samples used has contributed to colloid populations released into dispersion during the early stages of batch leaching experiments. End-over-end mixing of samples, as used on the Swiss programme, could contribute to colloid generation due to erosion on one hand and promote orthokinetic aggregation (agitation increases the rate and kinetic energy of particle collisions) of particles on the other. In addition, the flow rates used in column experiments on crushed material are significantly higher than would occur in a repository and may also contribute to erosion. The use of experimental solid to liquid ratios (typically 1:5 to 1:100) that are much lower than would arise in a repository (less than 1), may tend to increase colloid populations compared to porewaters due to reduced particle-solid interactions. Thus, overall it is expected that colloid populations generated in experiments may be enhanced compared to



repository conditions. However, despite these limitations of the experimental methods, there is no indication of significantly high colloid populations being generated as a result of the procedures used.

The colloid concentrations measured in short-term, small-scale laboratory examples are supported by low colloid concentrations  $(1-5 \times 10^{10} \text{ particles dm}^{-3})$  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 contention 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 the dominant colloid generation mechanism from the bulk material in the longer-term leaching experiments.

Two combined waste equilibrium leach tests (ELTs) have shown that a range of colloid types may arise from interactions of cement materials with waste components; however, measured leachate colloid concentrations in supernatant leachates were also low, about 10<sup>10</sup> particles dm<sup>-3</sup>, (100 - 5000 nm size fraction) for supernatant leachates and less than 10<sup>11</sup> particles dm<sup>-3</sup>, (100 - 5000 nm size) for drained leachates, in common with batch leaching experiments on cured NRVB.

The possible effects of organic compounds derived from waste form materials have been investigated both directly and indirectly in a small number of experiments. Leaching of the M1 backfill in the presence of ISA, the major degradation product of cellulose under alkaline, anaerobic conditions, indicates that sorption of ISA onto the backfill does have an effect in stabilising colloid population and reducing the rate of colloid aggregation. However, the effect is too small to have a significant effect on colloid populations in the long-term. This finding is supported by the low colloid populations measured in the ELT and microcosm tests that included both cementitious materials and real or simulated wastes. There is no indication for enhanced colloid populations in these tests over the experimental timescales (2-6 years) as a result of colloid-organic compound interactions.

There is little information available concerning the potential effects of natural organic materials in particular, alkaline soluble fulvic-like materials, on near-field colloid populations. At Maqarin where humic substances were found to be absent and dissolved organics comprised predominantly aromatic species there was no evidence of cementitious colloid interaction with organics. However, fulvic-like materials are known to stabilise colloidal particles in near-surface waters and may be more significant in their effects on inorganic colloid stability than waste-derived organics. Natural organic populations will be site-dependent and as such are a site-specific issue.
### 3 Stability behaviour of colloids in the near field

### 3.1 Introduction

In this Section, the current understanding of the stability of colloids in the near field of a cementitious repository is reviewed. On the basis of the near-field colloid decision tree presented in Figure 1.2, there are three key questions of interest:

- Are typical groundwater colloid populations stable in the near field?
- How stable are colloid populations generated within the near field?
- Do colloid populations in the near field interact with the surfaces of the backfill and other near-field materials?

It was noted previously (Section 1.5) that there is a strong relationship between the presence of colloids in the engineered systems and their stability, because stability may be the determining factor controlling the concentrations and compositions of colloids in groundwater systems and in the near field. Likewise, stability may also be a key factor in determining the colloid populations measured in experiments. In this Section, the focus will be on the phenomenological understanding of colloid stability under near-field conditions. It should be noted that this understanding is built firmly on existing knowledge of colloid behaviour, developed over many years in the field of colloid science.

In Section 3.2, the factors controlling colloid stability will be discussed. In Section 3.3 experimental methods for studying colloid stability will be outlined and in Sections 3.4 to 3.6 existing knowledge from experimental studies will be reviewed. The interpretation of the experimental results will be discussed in Section 3.7 and the current understanding of colloid stability under near-field conditions summarised in Section 3.8

### 3.2 Factors determining colloid stability

Two types of colloid 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 concerns the stability of the dispersion as a whole towards aggregation as a result of particle collisions in the liquid medium.

### 3.2.1 Chemical stability

Inorganic colloids are thermodynamically metastable with respect to bulk solid phases [148, 149]. 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 be significant over the longer timescales relevant to radionuclide transport in the near field of a GDF and through the geosphere. It follows that colloids must be composed of phases with low solubility in the solution in which they are suspended (and often, but not in all cases, have slow dissolution kinetics) if they are to remain as colloids for long periods. Thus any colloid, even under steady state chemical conditions, may have a finite lifetime [55] determined by its size and rate of dissolution and this obviously has significant implications for radionuclide transport.

Particles that are composed predominantly of redox sensitive elements (e.g. Fe(III) or U(VI) oxides) may be reduced or oxidised if exposed to a change in redox conditions. Indeed,

serco

colloidal Fe and S are often observed in the immediate vicinity of redox fronts [e.g. 59], although these may be by-products of microbial activity.

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 <sup>14</sup>C-dating [150].

### 3.2.2 Physico-chemical stability

The principal mechanism of inorganic colloid stabilisation against aggregation is electrostatic repulsion. Colloids 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 atmosphere of counterions. This spatial separation of charge is called an electrical double layer.

Physico-chemical stability of colloids depends on:

- electrostatic interactions arising from surface charge and double layer interactions;
- London-van der Waals attraction;
- hydration the structuring of water layers at the colloid surface; and
- steric repulsion the presence of natural organic macromolecules on colloidal surfaces which may also prevent colloids approaching sufficiently closely to aggregate [151].

The Derjaguin and Landau [152], Verwey and Overbeek [153] (or DLVO) theory for colloidal stability combines the effects of the van der Waals attraction and the electrostatic repulsion due to the electrical double layer and forms the theoretical framework for understanding colloid stability. It is still widely used today to predict some colloidal interactions, such as the collision efficiency factor [e.g. 154], but it has quantitative limitations under conditions where rates of colloid aggregation are low [155] or when chemical reactions such as sorption of organic species are involved [e.g. 156]. The DLVO theory can be applied to understand both colloid-colloid interactions and the interactions of colloids with surfaces.

Colloidal particles in dispersion are in continuous motion due to Brownian diffusion and in a flowing system will be transported in the water. As a result, particles will regularly collide. During collisions between particles of similar surface charge, overlap of the diffuse parts of the electrical double layers will cause repulsion. However if the particles approach closely enough, van der Waals attractive forces will pull the particles into contact. This combination of short-range attractive forces and longer range electrostatic repulsion produces an energy barrier to particle contact. If the resulting energy barrier is higher than the kinetic energy of the particles, they will be prevented from coming into contact to form an aggregate. The extent of double layers and the height of the energy barrier to aggregation is controlled by the solution ionic strength and, particularly the valency of counterions (polyvalent ions coagulate colloidal dispersions at lower electrolyte concentrations than monovalent ions). As the ionic strength is increased, a point is reached at which the net energy barrier is reduced to zero. At this point, known as the critical coagulation concentration (CCC), the system should coagulate rapidly with all colloid-colloid contact resulting in aggregation.

On the basis of approximate equations for the electrostatic and van der Waals interactions between two identical spheres (which will be presented later in sub-section 3.7) and the conditions that both the net interaction potential and potential gradient are zero at the CCC, two expressions for the relationship between the surface potential  $\Psi$ , the counter ion valency, *z*, and the CCC can be derived. CCC values are predicted to be proportional to  $1/z^6$  at high surface

potentials and  $\Psi^4/z^2$  at low surface potentials (typically < ±50 mV). In general, experimental data for the aggregation of model colloid systems for counter ions of different valency are in agreement with the  $1/z^6$  dependence predicted by the DLVO theory (this prediction is referred to as the Schultz-Hardy rule) [155].

The surface charging behaviour of oxide minerals depends on their composition and the protonation-deprotonation behaviour of surface hydroxyl groups. 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<sup>-</sup> 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 or PZC. Examples of PZC values reported in the literature for a range of minerals are presented in Table 3.1 [157]. The typical PZC value of 8.6 for synthetic haematite compares with a value of 4.8 for a natural haematite (which is thought to have a lowered PZC due to silica contamination).

### Table 3.1 Point of Zero Charge (pH Value) for some Oxide Minerals and Calcite [157]

Mineral	Point of Zero Charge
Quartz, SiO <sub>2</sub>	2-3.7
Cassiterite, SnO <sub>2</sub>	4.5
Rutile, TiO <sub>2</sub>	6.0
*Haematite (natural) Fe <sub>2</sub> O <sub>3</sub>	4.8
Haematite (synthetic)	8.6
Goethite, FeO(OH)	6.9
Corundum, Al <sub>2</sub> O <sub>3</sub>	9.0
Magnesia, MgO	12
Calcite, CaCO <sub>3</sub>	9.5

\* Probably contaminated with SiO<sub>2</sub>

The implication of the data in Table 3.1 is that at high pH values (i.e.  $\geq$ 12), typical of the repository near field, common minerals will have negative surface charges (this includes clay minerals which have an intrinsic structural negative charge). Thus colloid stability will be controlled by the concentrations of metal cations in solution.

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 sub-section 3.3.3.

According to Hunter, there is a large body of experimental evidence showing that when rapid coagulation occurs in aqueous colloidal systems, the measured zeta potential is commonly in the range ±25-50 mV [158].

At electrolyte concentrations below the CCC, particle aggregation may still occur when colloidcolloid interactions have sufficient kinetic energy to overcome the energy barrier. The fraction of particle collisions that result in particles sticking together is predicted to decrease very rapidly



with decreasing electrolyte concentration below the CCC [159]. This tendency for particles to aggregate is often expressed as the attachment factor or sticking probability, denoted  $\alpha$ , which is defined as the ratio of the rate of coagulation under a given set of experimental conditions, to the ratio of fast coagulation when there is no energy barrier to coagulation (by definition,  $\alpha \leq 1$ ).

Particle aggregation is not necessarily an irreversible process, however. 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 polyvalent co-ions [160].

It should be noted that the structure of the colloid's surface can significantly alter the intercolloid forces and modify stability, effects that are not accounted for in the DLVO theory [155]. Hydration may lead to additional short-range repulsive forces during colloid-colloid interaction, which may increase their stability [161]. It has been reported that these forces may restabilise colloidal dispersions at electrolyte concentrations above the CCC [162].

The presence of a gel-like layer of protruding silanol and silicic acid groups at silica surfaces appears to provide an explanation [163] for the anomalous stability of silica colloids towards aggregation [164] and other unusual surface properties of silica.

The presence of adsorbed material on colloid surfaces can modify surface properties and stability. For example, the sorption of polyvalent cations can reduce the surface charge of (negatively charged) colloids, reducing their stability and even reversing their charge [e.g. 165]. There is evidence for charge reversal of mineral colloids at high pH in the presence of high concentrations of calcium ions [70, 166]. Indeed, the measured zeta potentials of a number of important cement minerals, such as calcium hydrate silicate (CSH) gels may be positive at high pH [167, 168].

There is extensive evidence from fresh, estuarine and marine waters that the surface charge and colloidal stability are controlled by natural organic matter [e.g. 169]. This has been attributed to the influence of sorbed humic substances on surface charge. Alternatively, at low organic concentrations, macromolecules may sorb onto two separate colloids and cause them to flocculate (known as bridging flocculation [170]).

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.  $Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$ ) [160].

### 3.3 Experimental methods

### 3.3.1 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 scattered light intensity or turbidity or measuring changes in particle size distribution by PCS (see sub-section 2.2.5). 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<sup>3</sup>) 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 for near-field colloids in cementitious systems (see Table 2.2). 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 stimulant systems may be obtained from commercial sources (e.g. colloidal silicas), prepared in the laboratory from standard recipes (e.g. haematite colloids [171]) or prepared by crushing/disaggregation and dispersion (e.g. with ultrasound) from bulk materials, such as cured cements. The first two sources have the particular advantage that dispersions can be obtained or prepared with known shape and with relatively uniform particle size. Standard clay minerals are available from the Source Clay Repository of the Clay Minerals Society [172]; colloidal sized clay fractions can be separated by re-dispersion and progressive centrifugal sedimentation of larger sized fractions.

The lower the sample concentration, the longer the timescales over which aggregation will occur (see Table 3.2 below). Studying colloid stability in cement leachates, for example, generally requires periodic sampling and examination by more sensitive characterisation techniques such as single particle counting (e.g. [9]) or TEM/SEM (e.g. 19,98].

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 near-field porewater [26,70,166].

### 3.3.2 Particle deposition studies

The interactions of colloidal particles with surfaces have been the subject of extensive experimental investigation in colloid science since the mid-1960s (see for example reviews by Adamczyk [173] and Jia and Williams [174]). Studies to understand the mobility of colloids in the environment have been undertaken since the 1980s and have included colloid transport experiments in porous media (column experiments) and through fractures; experiments have been undertaken both in the laboratory and in the field. Relevant work on the Nirex programme (under geosphere-relevant conditions) is reviewed in [19].

Little work has been undertaken to study colloid interactions with surfaces under near-field conditions, except for one column type experiment has been described by Gardiner *at al.* [70] (see section 3.5).

#### 3.3.3 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 [175]. 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 microelectrophoresis techniques [176]. In simple terms, charged particles dispersed in an electrolyte solution are caused to migrate under the influence of an applied electric field. The dispersion is illuminated with a suitable light source and viewed through a microscope. The electrophoretic mobility of individual particles is determined by measuring their velocity. This type of measurement is highly labour intensive, requiring no small patience and skill (and good



eyesight) to record data for a sufficient number of particles within a dispersion to gain a meaningful average. It is also limited to particles that can be visualised microscopically, usually greater than about 0.5 µm in size. Since the late 1980s, these manual measurements have been largely superseded by laser-based electrophoretic light-scattering techniques. In this case, the light source is a focused laser and the frequency of the scattered light is measured using a photomultiplier. The electrophoretic mobility is determined from the Doppler shift of scattered light arising from the particles migrating in an oscillating electric field (see the reviews in [177, 178] for example for further information). Electroacoustic techniques have also been developed [179, 180], which can be applied to more concentrated samples that are not transparent to light, such as cement pastes.

In the context of the near field, electrophoretic mobility measurements have been used to study the charging properties of cementitious materials as a function of pH, ionic strength and the concentration of specific ions (such as calcium) or organic materials [e.g. 70,98,167,168,181]. The technique has also been used to study the characteristics of simulant near-field colloids [98] and model colloid systems [e.g. 26,166] under near-field conditions.

### 3.3.4 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 [182] and the atomic force microscope (AFM) [e.g. 183,184]. These techniques have been used to measure intersurface forces using model systems with well-defined geometries. Some AFM work has been undertaken on cement systems; for example, Uchikawa *et al.* [185] have utilised an AFM to measure the interactive force between the surface of cement clinker and an adsorbed admixture.

### 3.4 Colloid aggregation studies

### 3.4.1 Near-field colloids

Fujita *et al.* [98] investigated the stability of colloids generated from HFSC hydrate as a function of calcium concentration by aggregation studies using PCS. Owing to the small numbers of colloids generated in leaching tests (see Table 2.3) and the similarity in composition of the particles observed in leachates to bulk HFSC, colloidal particles of HFSC (with mean diameter about 300 nm) were generated by ultrasonic disaggregation of crushed cured material in distilled water. The resulting suspensions were allowed to settle for 1 day to allow coarse particles to settle before separation of the colloidal phase. Ca(OH)<sub>2</sub> solution was added to aliquots of the dispersions to give the required calcium concentrations and the particle size distribution was measured as a function of time to follow aggregation. For cases where the Ca concentration was below  $2 \times 10^4$  mol dm<sup>-3</sup>, little change was observed in the size distribution over 24 hours. However, above  $5 \times 10^4$  mol dm<sup>-3</sup>, aggregation of the particles proceeded rapidly. These results showed that the CCC for 300 nm HFSC colloids lies at a Ca concentration of about  $5 \times 10^4$  mol dm<sup>-3</sup> or below. This concentration is expected to be significantly less than Ca concentration in near-field porewaters and therefore the HFSC-derived colloids are not expected to be stable in the near field.

In the colloid generation experiments undertaken at PSI on the M1 mortar backfill [9] (see Section 2.3) and quartz grains in fresh cement porewaters (pH 13.3) particle concentrations were recorded as a function of settling time, firstly 1 hour and 24 hours after end-over-end shaking and then in later stages of the experiments periodically on undisturbed leachates. Samples collected after 1 hour represented all particles greater than 100 nm in size that sediment less than 6.8 cm (the sampling depth below surface) in 1 hour. Those collected after 24 hours represented all particles between 100 nm and 1000 nm in size. The differences between the two measured concentrations could be explained in terms of sedimentation, only, of the >1000 nm size fraction. Samples recorded after cessation of agitation showed drops in



colloid concentrations at the measuring height of up to 2 orders of magnitude compared to the 24 hour samples (typically about 2-8 particles dm<sup>-3</sup>). Similar results were obtained with M1 mortar and quartz grains. The drop in concentration was faster than that predicted for sedimentation of the particle size distribution measured after 24 hours alone, and this was attributed to an aggregation-sedimentation process controlling the colloid inventory. The kinetics of this removal process appeared to be relatively fast, background levels of colloid concentrations for the system being reached within 20 days. The presence of ISA was found to retard the colloid removal process by a factor of about 2 but not appreciably in terms of long-term behaviour. In these experiments the high ionic strength of the systems (0.3 mol dm<sup>-3</sup>) rather than the calcium concentration, appeared to be the factor controlling colloid aggregation rates (i.e. at the high alkali metal concentrations, the presence of calcium had no additional effect).

### 3.4.2 Model colloids

Gardiner *et al.* [166] investigated the stability of model haematite colloids as simulants of colloids generated from the corrosion of iron-containing wastes and repository materials. For this study, a synthetic dispersion of spherical haematite particles with a mean size of about 170 nm was used. The colloids were initially dispersed in Volvic water (calcium concentration about 2.4  $10^{-4}$  mol dm<sup>-3</sup>) at a concentration of about  $10^{13}$  particles dm<sup>-3</sup>. The pH, though not recorded would have been near neutral. The aggregation of the colloids was followed with time by PCS following additions of varying amounts of a 3:1 BFS/OPC cement-equilibrated water (CEW, from 0 to 7.5% by volume). The dispersion was stable in Volvic water over the timescale of the experiments (1-3 hours) but the addition of just 2% CEW induced aggregation. Increasing the amount of CEW increased the rate of aggregation. Unfortunately, the pH and compositions of the CEW were not recorded.

The above series of aggregation experiments were repeated but using haematite dispersed in either a 100ppm solution of humic acid (Aldrich) in Volvic water or with the leachate from the alkaline degradation of wood (oak), with 100 ppm TOC, to represent the degradation products from cellulosic wastes<sup>8</sup>. The stability of the haematite was increased in the presence of both organic materials with no aggregation being detectable at CEW addition up to 5% and 7%. This stabilising effect of humic acid and oak leachate was suggested to be due to steric repulsion between adsorbed organic layers on the haematite as particles collide.

While the above results demonstrate destabilisation of model haematite colloids in contact with small amounts of a simulated near-field water and a stabilising effect of the organic materials, in the absence of pH and water composition information it is difficult to put these results into proper context.

Ramsay *et al.* [26] investigated the potential stability of three model groundwater colloids, silica (80 nm), kaolinite and montmorillonite (both  $\leq$  200 nm) on passing into a calcium-rich near field. Colloid stability, in terms of mean particle size measured by PCS, was studied as a function of added calcium hydroxide concentration. Aggregation was indicated by a marked increase in measured particle size. Silica and kaolinite were destabilised at calcium concentrations above 5 10<sup>-4</sup> mol dm<sup>-3</sup>, montmorillonite at about 10<sup>-3</sup> mol dm<sup>-3</sup>. Thus, these pure mineral colloids are expected to coagulate and be immobilised by sedimentation or surface attachment on entering the ADZ. Again, however, there is no record of the pH ranges associated with these experiments, or the timescales over which aggregation was measured to put them into wider context.

<sup>&</sup>lt;sup>8</sup> 100g of oak was extracted at 4°C for four weeks in 0.1 mol dm<sup>-3</sup> NaOH solution. The leachate, after filtration through a 0.45  $\mu$ m filter, was found to contain approximately 5000 ppm total organic carbon (TOC). The filtered leachate was used in the experiments.



Degueldre presents the results of batch aggregation tests carried out with montmorillonite colloids to determine attachment factors (or sticking probabilities) 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 [55], 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,  $\alpha$ , 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 3.11.

Similar to the results of Ramsay *et al.* [26], 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<sup>-3</sup>. In the absence of calcium, in line with the Schulze-Hardy rule, a significantly higher concentration of monovalent cations (Na, K), >10<sup>-2</sup> mol dm<sup>-3</sup> was required to induce aggregation .



Figure 3.1 The effect of monovalent (Na, K) and divalent (Mg, Ca) cation concentrations on the attachment factor, *α* (here denoted a), for montmorillonite colloids; the arrows denote decreasing stability [54]. Experimental conditions: colloid size ≥100 nm, initial colloid concentration 10 mg dm<sup>-3</sup> with pTOC <4.3 and pH 8.0, precision ±20%

### 3.4.3 Humic acid

The stability of a humic acid extracted from the Boom Clay (in 0.1 mol dm<sup>-3</sup> NaOH) to calcium was investigated in ultrafiltration studies [26]. Calcium concentrations greater than  $10^{-3}$  mol m<sup>-3</sup> were sufficient to precipitate the major portion of the humic acid. However, up to 25% of the total organic carbon, ~40 mg dm<sup>-3</sup> remained in solution after 7 days and passed a 0.22 µm filter. This calcium-stable fraction is most likely to be the low molecular weight fraction of humic material, referred to as fulvic acids. Although the Boom Clay is a humic-rich material, the



implication is that while higher molecular weight humic acids will be unstable in the near field, fulvic acids are soluble at high pH and may be mobile in the near field. It is not clear to what extent attachment of fulvic acids may occur to near-field materials.

### 3.4.4 Equilibrium leach tests

Although the two ELTs (described in detail in sub-sections 2.1.5 and 2.3.1) did not include aggregation studies *per se*, colloidal fractions in the equilibrium leachates and in fines-containing leachates were characterised 3 months after sampling [30] and then after about 15 month's storage [23,31]. The results allow a qualitative assessment of the stability of the colloidal size fractions derived from these tests to be evaluated.

An indication of colloid concentrations in the stored leachates is given not only by the measured colloid concentrations but also by the  $\alpha$ -activities. It was clearly established that the  $\alpha$ -activity was associated predominantly with colloids and particulates and dissolved  $\alpha$ -activities were negligible. It will be recalled that after sampling of the liquid phase in the stored bottles after 15 months, the liquid phase was decanted and the storage bottles were washed and treated with ultrasound to recover sedimented and wall-sorbed material. Additional sets of filter samples for gross  $\alpha\beta$ - and SEM analysis were prepared from the wash solutions. The results are presented in Table 2.5.

Compared to the original leachate activities, substantial releases of activity were found in the wash solutions from the heater-well leachate and equilibrium leachate sample bottles ELT1/H/US, ELT2/H/US, ELT1/A/US and ELT2/A/US. Measured colloid concentrations in these wash solutions ranged from a factor of 5 to a factor of 30 higher than in the original leachates sampled after 15 months. In addition, measured  $\alpha$ -activities in the wash solutions from the equilibrium leachates (ELT1/A/US and ELT2/A/US) were higher than the  $\alpha$ -activities measured in the leachate samples analysed after about 3 months by factors of at least 3 and 10, respectively, indicating that significant deposition had occurred prior to 3 months. Unfortunately, it is not possible to distinguish whether deposition had continued during the further year's storage owing to limitations of the data collected after 3 months.

In comparison, less activity was released by washing the bottles that had contained the topsurface leachates ELT1/V and ELT2/V than had been measured in original leachates. Wash solution  $\alpha$ -activities were lower by factors of about 2 and 6, respectively. Unfortunately, samples for SEM analysis were not prepared for these two solutions. Somewhat surprisingly, the results indicate that colloidal dispersions prepared from re-distribution of solid fines from the top surfaces of the tests were significantly more stable than colloid populations in the overlying leachates. In particular, a stable dispersion of brucite particles with a number concentration of at least 3 10<sup>11</sup> particles dm<sup>-3</sup> was produced in ELT2/V, whereas little brucite was found in the equilibrium leachates ELT2/A. In contrast, no brucite (derived from corrosion of the Magnox components of the waste) was identified by EDX in any of the leachate samples from ELT1 that contained a significant amount of NRVB.

The possible reasons for the lack of brucite particles in the ELT2 equilibrium leachate are discussed in reference [31] and may have been associated with evaporative losses, and possible drying out, that affected ELT2 during its operation. Clearly, brucite particles had been mobilised in ELT2 and had been deposited at some stage on the top-surface of the solids in the test. It appears that the chemical conditions in ELT1 were sufficiently different in the presence of NRVB (which doubled the solid content of the test) that significant mobilisation of brucite did not occur.

### 3.5 Colloid deposition study

The only example of a colloid migration experiment under simulated near-field conditions that has been found is a pair of column experiments reported by Gardiner *at al.* [70]. The migration



of <sup>59</sup>Fe-labelled haematite colloids applied to the tops of two columns containing a 0.5-1 mm in size fraction of crushed 3:1 BFS/OPC grout was investigated. Periodic sample removal from the bottom of each column (and replacement with like volumes at the top) found no detectable <sup>59</sup>Fe even after about 4.7 pore volumes had been eluted. Analysis of slices at the end of the experiments found that the majority of haematite was retained in the first 6 mm of one column and the first 12 mm of the other, with only small amounts recovered throughout the rest of the column. Recovery of the <sup>59</sup>Fe was not quantitative, however; up to 22% of the haematite in one column and 6% in the other was unaccounted for. It was inferred that these hematite fractions had passed through the column and were retained by the 35 μm pore size bed support. Unfortunately, no leaching of the columns to confirm this was undertaken.

The results were interpreted as retention of the haematite at the top of the column either due to attachment to the immobile cement surface or by the formation of larger species that could not migrate through the void volume. Such species could be formed either by aggregation of the haematite or interactions with colloids derived from the cement. It was speculated that the fractions of haematite that appeared to be mobile had probably passed through a few large voids (i.e. wider pathways) in the column. However, given that the uncertainties in the <sup>59</sup>Fe balance were not evaluated and the absence of experimental confirmation, the actual presence of a mobile fraction appears to be uncertain.

### **3.6 Studies of surface properties**

### 3.6.1 Cement phases

Numerous studies have been reported in the literature concerning the surface charge properties of cementitious materials and cement component minerals [e.g. 167,168]. Many of these studies have been concerned with understanding the rheological behaviour of cement slurries, prior to setting and the role of admixtures [e.g. 43,181].

In general, the zeta potentials of Portland cements have been reported to be weakly negative, at -12 to -15 mV [43], although Nagele, in particular, reported positive values between +5 and +20 mV [167,168]. The addition of superplasticisers (calcium lignosulphonates) has been shown to develop an increasingly negative zeta potential on cement particles, typically -20 to -40 mV depending on the type and amount of admixture used [43].

Gardiner *et al.* [70] measured the zeta potential of crushed and ultrasonically dispersed 3:1 BFS/OPC grout. In water equilibrated with the cement, the zeta potential was found to be positive (+15 mV), whereas on dispersion in 0.001 mol  $dm^{-3}$  sodium hydroxide solution the potential decreased to -45 mV. This change was ascribed to the desorption of excess calcium ions from the cement surface.

Fujita *et al.* [98] measured the zeta potentials of a number of cured cementitious materials including CSH gels with different calcium to silicon ratios. Pulverised samples were leached in de-ionised water at five S/L ratios (from 1:10 to 1:200) at room temperature for 80 days to reach dissolution equilibration. Electrophoretic mobilities of the particles at each S/L were measured by a laser-illuminated micro-electrophoresis method.

For OPC, 9:1 BFS/OPC and HFSC, equilibrated pHs at all S/L were >12.5, 12.0 to 12.3 and about 11.0 respectively. Equilibrated calcium concentrations were about  $2 \, 10^{-2}$  mol dm<sup>-3</sup> for OPC, 5 to 8  $10^{-3}$  mol dm<sup>-3</sup> for 9:1 BFS/OPC and 1 to 3  $10^{-3}$  mol dm<sup>-3</sup> for HFSC. The zeta potentials for both OPC and 9:1 BFS/OPC were found to be positive under these conditions, with zeta potential increasing slightly with increasing S/L ratio: +25 to +45 mV for OPC, +15 to +22 mV for 9:1 BFS/OPC. In contrast, HFSC particles were found to have a negative zeta potential (-20 to -25 mV) at each S/L. The zeta potentials of CSH phases were found to increase with increasing Ca/Si ratio; zeta potentials were positive for Ca/Si of 1.4 (+2 to +10 mV) and 1.65 (+20 to +30 mV) but negative for ratios of 1.1 and below (typically -10 to -



20 mV). Although not reported, equilibrated pH values for these CSH-gels would have ranged from about 11.3 at Ca/Si = 0.65 to pH 12 at Ca/Si = 1 to pH 12.5 at Ca/Si > 1.5). The Ca/Si ratio of bulk HFSC is about 0.86.

### 3.6.2 Near-field colloids

No measurements of electrophoretic mobilities of cement-derived colloids have been reported as colloid concentrations generated in leachates have been too low. However, the values reported above for cement phases may be considered as representative of the values for the types of colloids that will arise from disintegration of cementitious materials.

### 3.6.3 Model colloids

Gardiner *at al.* [70,166] have measured the zeta potentials of simulant corrosion product colloids at alkaline pH and as a function of calcium concentration by micro-electrophoresis. Zeta potentials were measured for suspensions of magnetite, haematite and zirconium hydroxide in 0.001 mol dm<sup>-3</sup> sodium hydroxide solution that were progressively diluted with cement-equilibrated (3:1 BFS/OPC) water (CEW). In sodium hydroxide solution both iron oxides possessed negative surface charges. Dilution with only small amounts (<1% for haematite) of CEW led to a charge reversal of the iron-based colloids due to specific adsorption of calcium ions. These experiments were undertaken at pH values close to 11, although values were not reported. In contrast, measured zeta potentials of zirconium hydroxide remained negative, even in CEW. The zeta potential apparently reached a maximum value (of -50 mV) at 10% added CEW. This behaviour may represent a balance between specific sorption of calcium and increased dissociation of Zr-OH sites at the hydroxide surface as pH is increased.

Some additional measurements using haematite onto which plutonium or americium had been sorbed in batch experiments (see sub-section 4.3.2), found that the sorbed actinides did not alter the (negative) zeta potentials within experimental error.

These results were interpreted to indicate that the surface properties of the corrosion product colloids in the near field will be controlled by the specific sorption of cations, in particular calcium, rather than trace quantities of radioelements leached into the porewater. Both haematite and magnetite surfaces would be expected to be positively charged under near-field conditions, of similar sign and magnitude to cement surfaces. Zirconium hydroxide surfaces appear to be negatively charged and therefore zirconium hydroxide colloids would be expected to be attracted to positively charged cement surfaces and not stable in the near field. Such behaviour has yet to be confirmed, however.

In a subsequent study [166], the zeta potentials of haematite particles in 3:1 BFS/OPC water adjusted to pH 11 were measured to range from about -10 to -25 mV. Ten times dilution with deionised water reduced the zeta potential further to  $-50\pm20$  mV due to the desorption of calcium. Ten times dilution with 0.4 mol dm<sup>-3</sup> sodium chloride solution was found to increase the zeta potential to essentially zero through suppression of double layer interactions.

Gardiner *at al.* [166] also measured the zeta potentials of haematite and magnetite at pH 12 in sodium hydroxide solution, in the presence of humic acid but in the absence of calcium. The magnitude of the zeta potential of haematite particles was increased from -60 mV to -90mV on addition of 20 ppm humic acid and to -120 mV at 100 ppm. The zeta potential of magnetite was highly negative (-100 mV) and was not affected by humic acid.

Flatt *et al.* [186] used commercial magnesium hydroxide and 'dead burnt' magnesium oxide powders as model particles for the investigation of superplasticiser adsorption onto cements. The iso-electric points for these materials are expected to be at pH 12.0 and 12.4 respectively [187]. Zeta potentials in 0.01 mol dm<sup>-3</sup> sodium hydroxide solution were weakly positive at +6 mV (at pH 11.3) and +10 mV (at pH 12), respectively.

### 3.7 Interpretation of experimental results

### 3.7.1 Understanding colloid stability under near-field conditions

The understanding of the physico-chemical stability of colloidal particles in the near field of a cementitious repository can be understood in terms of the electrostatic interactions between particles and between particles and surfaces on the basis of DLVO theory.

According to the DLVO theory, the total energy,  $V_T$ , of interaction between two colloidal particles is the sum of an electrostatic repulsion energy,  $V_R$ , and attractive energy,  $V_A$ , due to van der Waals-London dispersion force. The repulsion force  $V_R$ , between two spherical particles (radius *a*, separation distance between the particle surface *H* is approximately represented [188] by

$$V_{R} = \frac{\varepsilon a^{2} \varphi_{0}^{2}(H+a)}{H+2a} \ln \left[ 1 + \frac{a}{a+H} \exp(-\kappa H) \right]$$
(3.1)

where  $\kappa = (8\pi nZ^2 e^2/\epsilon kT)^{\frac{1}{2}}$ ,  $\epsilon$ : permittivity of medium,  $\varphi_0$ : Stern potential, *n*: density of ion, *Z*: valence of ions, e: elementary charge, *k*: Boltzmann's constant, and *T*: absolute temperature. The Stern potential can be replaced by the zeta potential. The attractive force,  $V_A$ , is represented by:

$$V_{A} = -\frac{A}{6} \left[ \frac{2}{s^{2} - 4} + \frac{2}{s^{2}} + \ln \left( \frac{s^{2} - 4}{s^{2}} \right) \right]$$
(3.2)

where s = (H/a)+2.

The constant *A* is referred to as the Hamaker constant and its value depends on the nature of the interacting materials. The calculation of Hamaker constants has been reviewed by Gregory [189] and values have been tabulated [190]. However, calculated values are often considered to be too high, and for specific systems may be determined from evaluation of coagulation data [175]. For the purposes of modelling experimental data, the Stern potential in equation (3.1) is frequently replaced with the zeta potential, which can be measured experimentally.

A number of authors have considered colloid stability in cementitious systems theoretically on the basis of DLVO theory. Yang *et al.* [191] considered the colloid stability of wet pastes of OPC. Both experimental and theoretical work showed that suspensions of OPC were flocculated or coagulated owing to the high ionic strength in the porewater and that the degree of flocculation would be insensitive to variations in zeta potential when it lies between -20 mV and +20 mV.

Although the conditions in near-field porewater will be somewhat different to those in hydrating cement pastes, the analysis of Yang is valid, nevertheless. The data presented in sub-section 3.3.3, indicates that most OPC components and crushed bulk OPC have zeta potentials under high pH conditions that fall within this range.

Fujita *et al.* [98] made a preliminary interpretation of the dependence of colloid concentrations of HFSC-derived colloids on the S/L ratio in leaching experiments (see Table 2.4) by applying DLVO theory. Electrophoretic mobility measurements of HFSC had shown that the cement surface has a negative charge under the conditions of the leaching experiments (pH ~11.3). Therefore, the stability of HFSC-derived colloids was expected to be controlled by the calcium ion concentration in solution.





Distance between particle surface, H / nm

Figure 3.2 Indicative interaction potential curves for leached colloid (a=25nm, the zeta potential=-25mV) from HFSC hydrate calculated at each Ca concentration (from [98])



Figure 3.3 The effect of groundwater compositions on natural colloid (>100 nm nominal size) concentrations; the arrows denote decreasing stability [54]. 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 - Bagombe (BAG2). Precision on colloid concentration about 10% The results of indicative calculations of the net interaction potential between two HFSC particles as a function of surface separation distance are shown in Figure 3.2.

It was found that for calcium concentrations greater than  $10^{-3}$  mol dm<sup>-3</sup>, the calculated potential curves had a positive potential barrier, which increased in height with decreasing calcium concentration. At a calcium concentration below  $10^{-3}$  mol dm<sup>-3</sup>, the positive peak on the potential curve disappears and rapid coagulation would be expected, i.e. the indicative CCC is about  $10^{-3}$  mol dm<sup>-3</sup>. It should be noted that owing to the relatively low potential barrier, even at  $10^{-4}$  mol dm<sup>-3</sup>, slow aggregation of the particles would be expected.

The calcium concentrations measured in leaching experiments at S/L ratios of 1:5, 1:50 and 1:100 were about  $3 \ 10^{-3}$  mol dm<sup>-3</sup>,  $10^{-3}$  mol dm<sup>-3</sup> and  $10^{-3}$  mol dm<sup>-3</sup>, respectively. In the experiments (Table 2.5), significantly higher number concentrations were found at low S/L ratios (1:50 and 1;100) compared to high S/L (1:5). Assuming that the colloidal dispersions were stable at the lower S/Ls, the lower number concentrations at the higher S/L ratios can be explained qualitatively by a change in aggregation behaviour due to the higher calcium ion concentrations in the leachate solution.

### 3.7.2 Understanding of colloid populations in terms of colloid stability

In the previous section, an example was given in which the measured colloid populations in HFSC leaching experiments could be correlated with the solution concentration of calcium, which in those experiments was controlled by the solid to liquid ratio. Examination of colloid populations measured in groundwaters has found similar correlations between measured colloid concentrations and the groundwater composition, in particular the concentrations of mono- and divalent cations. This is illustrated in Figure 3.3 which shows that colloid populations vary over about four orders of magnitude depending, in particular on the calcium (and/or magnesium) concentration. 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 3.1.

These results show that there is a strong correlation between colloid stability (in terms of the aggregation rate) and concentrations in natural groundwaters. The findings of the AEAT/CRIEPI work with HFSC suggest that this type of relationship also extends to higher pH cement-equilibrated waters.

Given that colloid aggregation is a second order process, for an initially monodisperse population of spherical particles, the change in the monodisperse fraction concentration ( $C_{col}$ ) with time can be expressed as [192]:

$$\frac{dc_{col}}{dt} = -\frac{4\alpha k_b T}{3\eta} c_{col}^2, \qquad (3.3)$$

where  $\eta$  is the solution viscosity, *T* is the temperature (in Kelvin) and  $k_{\rm b}$  is Boltzmann's constant, and  $\alpha$  is the attachment factor.

Solving equation (3.3), 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,  $\alpha$ , as follows:

$$t_{1/2} = \frac{3\eta}{4\alpha k_b T c_{col,g}} \,. \tag{3.4}$$

Degueldre [55] has used equation (3.4) 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<sup>-3</sup>. The results are reproduced in Table 3.2.

## Table 3.2 Calculated half-lives of colloid populations for monodispersed colloids of different size and concentration as a function of attachment factor, $\alpha$ (after [55])

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

Equation (3.4) 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.

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. In practice, the lifetime will be related to particle size through the attachment factor, which is itself particle-size dependent.

The above analysis provides a phenomenological basis for understanding why colloid populations in cement leachates are non-zero, despite the unfavourable conditions for colloid stability.

Although DLVO theory can be used to predict aggregation rates at high sticking probabilities, when conditions become less favourable to attachment and aggregation rates become slow, other factors not accounted for in the simple theory (variations in particle shape, surface roughness, inhomogeneities of surface charge) become important in controlling aggregation rates [155]. Since theory does not allow reliable calculation of attachment factors under less favourable conditions, aggregation rates must be measured. In addition, the simple theory does not allow for steric stabilisation effects that may arise from the sorption of organic materials. Thus evaluation of colloid particle lifetimes towards aggregation, ideally requires measurements of aggregation rates for the particular system and conditions under investigation. In practice, this would probably need to be done on the basis of periodic sampling of an experimental system (such as an ELT, for example), subsequent maintenance of the water samples under static conditions and their periodic sampling for colloid analysis.

### 3.8 Current understanding of colloid stability under near-field conditions

On the basis of DLVO theory for colloid stability, most of the types of colloid that may form in the repository near field as a result of erosion, spallation or re-precipitation processes are expected to be destabilised under the high calcium concentrations (above 10<sup>-3</sup> mol dm<sup>-3</sup>) that will be

maintained over very long timescales in the near field. Destabilisation will lead to aggregation and sedimentation of colloids and/or a tendency for colloids to attach to solid surfaces.

Measured zeta potentials for a range of cement minerals and for simulant near-field colloids in the presence of cement-equilibrated waters are typically below about  $\pm 50$  mV and usually less than  $\pm 25$  mV. These values are considered to be insufficient to stabilise colloids towards aggregation in the long term at expected near-field calcium concentrations.

Likewise, typical inorganic groundwater colloids, such as silicas and clays, are not expected to enter the near field in significant concentrations due to the gradients in calcium concentration experienced at the geosphere-near field interface.

This does not mean that near-field colloid concentrations are expected to be zero, however. It is considered that colloid populations will be present in near-field waters, potentially with locally variable compositions depending on the local chemical conditions that represent an equilibrium between colloid generation and loss processes. There is a growing body of evidence that colloid populations in deep groundwaters are controlled by the chemical composition of the groundwater, which controls the rates of particle aggregation [55]. The apparent correlation of colloid concentrations for HFSC leachates with calcium concentration reported by Fujita *et al.* [98] supports this view and suggests that the same processes will control colloid populations under high pH conditions.

Thus, in general, under conditions of low-groundwater infiltration rates and uniform repository temperature that will develop over long timescales, the high calcium concentration in the near field is expected to control inorganic near-field colloid populations to low levels. This is supported by the low colloid number concentrations seen in all of the colloid generation studies and the ELTs described in this report (Table 2.2).

A number of potential exceptions to the above rule should be mentioned, however.

The formation of a stable dispersion of colloidal brucite, apparently, at high pH reported by Evans *et al.* [31] remains unexplained. Given the high pH (12.2) and calcium concentration  $(3 \times 10^{-3} \text{ mol dm}^{-3})$  of the leachate in the test and an expected PZC for magnesium hydroxide of about pH 12 [187], the brucite particles would not be expected to be stable under the chemical conditions in the test. It is also notable that brucite colloids were not observed at all in the second test that contained NRVB. Although the latter observation is reassuring, given the large volume of waste Magnox in the UK inventory, some further work on the stability of brucite colloids would seem to be justified.

The second potential exception to the above rule may arise in the presence of organic materials that sorb onto surfaces in sufficient quantities to effect colloid stabilisation as a result of steric repulsion in addition to electrostatic repulsion.

Under far-field conditions, humic acids have been observed to sorb onto colloids, altering their zeta potential to more negative values and reducing aggregation rates. In general, the concentrations required to achieve this are significantly higher than would be anticipated in deep groundwaters. Although humic acids are not anticipated to enter the repository near field owing to their insolubility at high pH and high calcium concentrations, lower molecular weight fulvic acids may potentially enter and be stable in the near field. The nature of natural organic substances (as well as native colloid populations) in the groundwater that may potentially enter a repository is a site-specific issue and should be addressed in future site characterisation programmes.

As noted previously in Section 2.8, the presence of ISA at concentrations that may arise in waste packages was found to have an effect in retarding the aggregation of M1 mortar-derived colloids but not to have a significant effect on long-term colloid concentrations. Similarly the presence of an alkaline leachate of oak was found to increase the threshold concentration for



hematite aggregation on addition of cement-equilibrated water, but not to prevent aggregation at higher pH and calcium concentrations. Thus, limited experimental evidence to date does not seem to show cellulose-derived organic degradation products having a significant effect in controlling colloid stability under near-field conditions. However, there is a wide range of other organic materials present in a repository that either as-disposed or on degradation may give rise to surfactants that may affect colloid stability.

For example, the stabilisation of colloidal particles underlies the use of superplasticisers to improve the rheological properties of wet cement pastes (although owing to ongoing cement hydration reactions, this does not prevent setting of the cementitious materials). Superplasticisers are of concern principally where low-pH cements may be used as backfill material. This is not currently envisaged in the UK, where the high pH NRVB has been preferred. However, it is possible that superplasticisers by be used in grout formulations.

The degradation of organic waste materials is an area of ongoing research under the NDA RWMD programme. At this stage there is insufficient information available to assess whether surfactant compounds may arise in significant quantities, either in the repository as a whole or in niche environments, to impact on colloid stability. Therefore the potential for organic stabilisation of near-field colloids remains an area of uncertainty.

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# 4 Radionuclide uptake onto colloids in the near field

### 4.1 Introduction to sorption onto colloids

Radionuclides may, in principle, sorb onto the surfaces of inorganic colloids by the same processes of surface complexation and/or ion exchange by which they can sorb onto the solid surfaces of the near field such as cements or backfill materials. Although in general, sorption is regarded as beneficial to radionuclide retention in a repository, sorption to colloids may not be advantageous if the colloids are mobile and if the sorption is irreversible (cf. Figure 1.2). Radionuclides may also complex to organic molecules that are present as colloids or attached to inorganic colloids. Owing to the higher surface area-to-volume ratio of colloids compared to near-field solid materials, the specific sorption capacity of colloids is expected to be higher than for backfill or grout materials.

In general, radionuclides sorbed onto mineral surfaces are anticipated to be in thermodynamic equilibrium with the solution phase. However, there are a number of mechanisms by which sorbed species can be removed from the sorption equilibrium so that sorption is effectively irreversible over a given timescale [55]:

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

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

(iii) sorption into an internal (e.g. an interlayer) site;

and in the case of colloidal particles, specifically:

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

Whether these processes should be regarded as irreversible over timescales of relevance to performance assessments is open to question. For example, radionuclides that may become incorporated into a surface (crystallisation) following sorption may be released at a later time due to mineral dissolution (see discussion in sub-section 4.4).

A key point which emerges from examination of the international literature is that the prevailing view is that little work on sorption to near-field colloids is justified until a significant presence of colloids in the near field can be firmly established (as far as the authors can ascertain, near-field colloid sorption studies are currently ongoing only in the Japanese programme). In general, experiments carried out to date (Section 2) have shown low concentrations of colloids and, as a consequence, relatively little work on sorption to colloids under near-field conditions has been undertaken. The available data are presented here along with approaches used to assess the potential significance of radionuclide uptake to colloids in the absence of specific near-field data.

### 4.2 Methods

### 4.2.1 Batch sorption

The most commonly used method for studying the sorption of radioelements onto geological and cementitious materials is the batch sorption method. This technique measures the partitioning of an element between the solution phase and the surface of a crushed solid of interest. The radioelement is added to the solution phase to give a concentration that is below the solubility limit for that element under the experimental conditions. One or more samples of the solution phase are analysed at the outset of the experiments (before contact with the solid) to determine the initial radioelement concentration. The solution phase is then added to the



solid and equilibrated for the required time (which may vary from a few hours to many months and may entail the sample simply sitting on the laboratory bench or being agitated), a portion of the solution phase is then removed and passed through a pre-treated filter to separate the solution phase from any suspended solids. The final concentration of radioelement in solution is then analysed 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.

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. However, for sorption onto the colloidal phase to be clearly distinguished, concentration of the colloid dispersion may be required before use in the experiments.

In addition, the batch sorption method can be modified to study the desorption of radioelements from surfaces under equivalent or changing chemical conditions. This may be achieved by adjusting the solution chemistry (e.g. lowering pH by acid addition), dilution of the experiments with an equivalent equilibrated water or different electrolyte solution, or removing the solution phase and replacing with radioelement-free solution.

Only a small number of batch sorption/desorption studies of near-field colloid types at alkaline pH have been reported in the literature [27,70,166]. The results of these studies will be described in sub-section 4.3 below.

It should be remembered that in a 'real' colloidal system of relevance to radioactive waste, a third medium is usually present – i.e. the near field waste and backfill or the far field host rock. There will be competition for radionuclide uptake between the solid and colloid surfaces. In addition to adsorption processes, precipitation and co-precipitation processes may also occur. In such cases, the concept of  $R_d$  and  $K_d$  breaks down (see discussions in [193,194]).

#### 4.2.2 Equilibrium leach tests

Larger scale near-field simulation experiments such as equilibrium leach tests provide an ideal opportunity to study the association of radioelements with near-field colloids and particulates under simulated near-field conditions. To gain insight into radionuclide-colloid interactions investigation of both colloid populations and associated activities in the leachates is required. Such a study was undertaken during the destructive decommissioning of the two Nirex long-term equilibrium leach tests (ELTs), which are described in some detail in sub-section 2.1.5; the results of the activity analyses are outlined in sub-section 4.3.3 below.

### 4.3 Sorption of radionuclides onto colloids

Table 4.1 summarises published  $R_d$  values for radioelement sorption onto simulated near-field colloids measured in batch type sorption experiments. Compared to bulk cements and geological materials the dataset is scant and limited to the sorption of actinides. There is only one datum point for sorption to cement-derived colloids, which is a qualitative estimate only. Most of the data are for colloidal simulants of the potential corrosion products of metallic wastes including steels, Magnox and zircaloy. These data and the results of other studies that provide an insight into radionuclide association with near-field colloids are discussed in the following sub-sections.



### Table 4.1 Summary of sorption data for cementitious and corrosion product simulant colloids under near-field conditions

Colloid type	Element	рН	Water type	Rd values (cm <sup>3</sup> g <sup>-1</sup> )	Reference
NRVB-derived	U(VI)	12	Simulated saline NRVB-equil. water	>10 <sup>6 *</sup>	27
Haematite (130 nm)	Am	12	3:1 BFS/OPC–equil. water	$3  imes 10^{6}$	70
	Pu	12		$1 \times 10^5$	
Haematite (130 nm)	Pu	11	3:1 BFS/OPC–equil. water	2-9 × 10 <sup>6</sup>	166
Magnetite (450 nm)	Am	12	3:1 BFS/OPC–equil. water	$2 \times 10^{6}$	70
	Pu	12		$3  imes 10^6$	
Magnetite (450 nm)	Pu	11	3:1 BFS/OPC–equil. water	4-8 × 10 <sup>5</sup>	166
Magnesium hydroxide <sup>†</sup>	Am	11	3:1 BFS/OPC–equil. water	10 <sup>6</sup>	70
	12	12		$0.2-2 \times 10^{6}$	
	Pu	11		$0.5-2 \times 10^{7}$	
Zirconium hydroxide <sup>†</sup>	Am	12	3:1 BFS/OPC-equil.	1 × 10 <sup>7</sup>	70
	Pu	12	water	$2 \times 10^{6}$	

\* Qualitative estimate based upon assessment of supporting information.

<sup>†</sup> Precipitated hydroxide

### 4.3.1 Cementitious colloids

### a) OPC-derived particulates

In early work undertaken by Ramsay and co-workers [25,26] no attempt was made to measure sorption of radioelements onto cementitious colloids directly. However, evidence for enhanced leaching of radioelements due to association with released particulates was sought by the leaching of OPC pellets that contained significant levels (0.5% by weight) of a number of radioelements (Co, Ni, Ce, Eu, Th and U). After 39 days, an ambient temperature leachate was clear with no evidence of deposited solids on the walls of the flask. In contrast, marked deposits were observable on leaching at 60°C. Levels of radioelements associated with leachate and solid deposits combined from the 60°C experiment were enhanced compared to the room temperature leachate by 2-3 orders of magnitude for Ce, Th and U, one order for Eu and Co and a factor of 2 for Ni. Unfortunately, no attempt was made to understand the amounts of each element released in terms of solubility limitation or to compare the composition of the deposits to the bulk composition of the cured OPC.



### b) NRVB-derived colloids

Gardiner *et al.* [27] looked at the interaction between uranium(VI) and NRVB-derived colloids at pH 12. In this case, it was necessary to pre-concentrate the colloids. Litre batches of NRVB leachates were prepared by equilibrating crushed NRVB with simulated NRVB-equilibrated saline (RCF3 DET5) groundwater at S/L= 1:100 for 20 days at room temperature in a nitrogen atmosphere glove box. Each batch was pre-filtered through a 30  $\mu$ m pore size polypropylene pre-filter (Millipore (UK) Ltd) and then concentrated to about 70 cm<sup>3</sup> by retention above a 30,000 nominal molecular weight cut-off ultrafiltration membrane supported in a stirred cell. The typical pore size of such filters is 2-4 nm. Concentrates from each batch were combined; the leachate ultrafiltrates were used in colloid-free control experiments.

For the sorption experiments, a small volume of  $^{233}$ U-containing solution was added to a concentrated or ultrafiltered leachate to give a final concentration of U(VI) of about  $5 \times 10^{-7}$  mol dm<sup>-3</sup>, significantly below the solubility limit for U(VI) at pH 12 which had been measured to be  $4 \times 10^{-6}$  mol dm<sup>-3</sup> [195]. After equilibration periods of 6, 15 and 20 days, the colloidal phase was removed from the solution phase by centrifugal ultrafiltration through 30,000 NMWCO filters. The ultrafilters were then leached twice with acid to recover retained uranium. All solutions were analysed for  $^{233}$ U by alpha-spectrometry of prepared thin sources.

Results were similar after 6, 15 and 20 days equilibration; on average some 27% of the added uranium(VI) was associated with the colloidal fraction retained by the 30,000 NMWCO filter. In contrast, filtration of leachates through a 1.2  $\mu$ m pore size filter found no appreciable retention of uranium(VI) confirming that uranium(VI) was associated with particles of colloidal size that passed through the larger filter and not the particulate fraction.

By comparison, experiments with 0.5 ppm silica colloids dispersed in ultrafiltered NRVB-leachate showed no appreciable depletion of uranium concentration in true solution either because uranium (VI) binds relatively weakly to silica under saline near-field conditions or because the silica dissolves at the high pH.

Although this study clearly demonstrated the association of uranium(VI) with an NRVB-derived colloidal fraction, unfortunately, the concentration of NRVB-derived colloids in the concentrates was not measured directly, making quantification of an  $R_d$  value difficult. On the basis of qualitative arguments, based on estimated mean particle sizes (60 nm) and maximum concentrations of NRVB-derived colloids measured in leachates at that time and limits of detection for colloid particles of this size by PCS (no colloids were detectable in the colloid concentrates by PCS), an upper limit of the mass concentration of NRVB-derived colloids was estimated to be ~0.3 mg dm<sup>-3</sup>. By combining this value with the results of the sorption experiment, an estimated  $R_d$  value greater than 10<sup>6</sup> cm<sup>3</sup> g<sup>-1</sup> was obtained.

While the above arguments seem reasonable, there is clearly significant uncertainty concerning the actual mass concentration of NRVB-derived colloids used in the experiments and the estimated  $R_d$  value. Subsequent estimates (Table 2.2) of colloid concentrations from leaching crushed NRVB in demineralised water were less than  $10^{11}$  dm<sup>-3</sup> for the particle size range 15-1000 nm with a weighted mean particle size that is larger than 60 nm (which would be more readily detectable by PCS), both of which suggest that . Overall, however, it appears reasonable to assume that a value of  $10^6$  cm<sup>3</sup> g<sup>-1</sup> represents a lower limit for the  $R_d$  value for U(VI) sorption to NRVB-derived colloids. Such a value is significantly greater than values of  $6 \times 10^3$  cm<sup>3</sup> g<sup>-1</sup> measured for sorption of uranium (VI) onto freshly cured NRVB [195]. The increase in the  $R_d$  value is attributable to a significantly larger surface area available for sorption on the colloidal particles than for the solid phase. Differences in colloid composition compared to the bulk NRVB mineralogy may also be a factor [27].



### 4.3.2 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 and hence provide a transport mechanism. The sorption and subsequent desorption of plutonium and americium onto (and from) simulated corrosion products of iron, magnesium and zirconium have been studied using the batch technique [70]. The competitive sorption of these actinides between a BFS/OPC cement and some of these corrosion products was studied and mobility data obtained for the corrosion product colloids (see sub-section 3.6.3).

The actinides were found to be strongly sorbing on magnetite and haematite (simulated corrosion products of iron), zirconium hydroxide and magnesium hydroxide (Table 4.1) after equilibration for 6 days. Distribution ratios determined were greater than  $10^5 \text{ cm}^3 \text{ g}^{-1}$ , at least as great as those onto crushed 3:1 BFS/OPC. Competitive sorption experiments showed that sorption onto corrosion product simulants did not take place in preference to that on the cement or vice versa.

Desorption experiments were started immediately after sampling of the solution phase at the end of the sorption experiments. Desorption was studied under conditions that simulated the transition from a near-field porewater (at pH 11) to a far-field water (at pH 7). This was achieved either by adjusting the solution pH to 7, or by also diluting the sample 10-fold with either Analar water, a 0.4 mol dm<sup>-3</sup> NaCl solution or a 10 ppm humic acid solution. The actinide solution concentration was then remeasured after a further 6 days and new  $R_d$  values calculated. Only dilution of the near-field water with saline solution and adjustment of pH to a value of 7 was found to reduce  $R_d$  significantly (by a factor of 10) over the 6-day timescale of the experiments. In the other experiments, some desorption was observed to maintain the original high  $R_d$  values, but otherwise there was no significant change in the distributions.

Gardiner and co-workers also used a variant of the batch-sorption technique for further studies of actinide desorption [166]. In these experiments, the inventory of actinide added to the samples was increased by using the 'dissolving solid-in-filter' technique. In this method, the actinide is precipitated as a hydroxide within the body of an alkali-resistant ultrafiltration unit which is immersed in the aqueous phase containing the colloidal dispersion. The actinide solid is separated from the aqueous phase by the ultrafiltration membrane (a low NMWCO filter). This allows a flux of the actinide to diffuse into the experiment maintaining a solution concentration at or below its solubility limit. The determination of  $R_d$  requires measurement of both the total dispersed actinide concentration and the dissolved concentration using unfiltered and 30,000 NMWCO filtered samples, respectively. In addition, to enable the quantity of colloids to be determined accurately, zirconium and iron-based colloids radio-labelled with <sup>95</sup>Zr and <sup>59</sup>Fe, respectively, were used. The colloid concentrations could then be determined directly by  $\gamma$ -spectrometry.

The results of these high inventory experiments were difficult to interpret. Examination by these reviewers of the published data found that in all these experiments reported  $R_d$  values increased in the desorption step. This suggests that desorption from the colloids had not reached equilibrium over the one-month timescale of the experiments, i.e. that desorption kinetics were slow, contrary to the conclusions reached by Gardiner *et al.* [166].

### 4.3.3 Equilibrium leach tests (ELTs)

The association of radioelements with near-field colloids and particulates has been investigated in two long-term equilibrium leach tests (ELTs), which are described in some detail in Section 2.1.5. In these tests, the gross  $\alpha$ - and  $\beta$ -activities associated with 0.1 - 5.0 µm filtered colloid fractions were measured directly on filter samples prior to analysis by SEM. During initial colloid analysis [30], gross  $\alpha$ - and  $\beta$ -activity and  $\gamma$ -spectrometry was applied to both unwashed



filter samples prepared from the equilibrium leachates and washed filter samples prepared from suspensions of fines concentrates taken from the top surface and the heater well in each test. More detailed radiochemical analysis of dispersible fines was also undertaken using  $\alpha$ - and  $\gamma$ -spectrometry [30]. In addition, the radionuclide uptake in the top cementitious layer in each test was investigated to provide information on sorption processes occurring in the tests.

Further activity measurements were made after 15 months storage of the leachate samples prior to colloid analysis by SEM; gross  $\alpha$ - and  $\beta$ -activity analysis of filter-retained colloid fractions was undertaken for each ELT leachate and fines sample and on wash solutions from each sample bottle [31,23]. These results are included in Table 2.5.

As noted previously (see sub-section 2.3.2), relatively few particles were found in 0.1 - 5.0 µm filter-retained colloid fractions of the equilibrium leachates after storage for 15 months. Negligible levels of  $\alpha$ -activity were associated with this stable colloidal phase. However, higher  $\alpha$ -activities were associated with colloidal and particulate material recovered from the storage bottles following ultrasonic treatment: 5.5 and 60 Bq dm<sup>-3</sup> for ELT1 and ELT2 respectively, and these figures were considered to provide estimates of the colloid associated  $\alpha$ -activities present in the equilibrium leachates at the end of the tests. In contrast, the amount of colloid-sorbed  $\beta$ -activity (<sup>90</sup>Sr) was negligible compared to dissolved activities.

Radiochemical analysis of the bulk supernatant leachates collected from each ELT at the ends of the tests were undertaken on 0.45 µm-filtered solution fractions [30], which is likely to have included the smaller size fractions of colloidal particles. The actinide concentrations were found to be below estimated solubilities in near-field porewater; the total  $\alpha$ -activities were estimated to be 3.3 and 2.2 Bq dm<sup>-3</sup> for ELT1 and ELT2 respectively. Unfortunately, solutions were not filtered through finer pore-sized filters, such as 30,000 MWCO ultrafilters, to investigate the actinide distribution between true solution and association with the finer colloid fraction.

From comparison with expected actinide near-field solubilities, it was concluded in [30] that there was little evidence for a significant actinide burden for the colloid fraction that is <0.45 µm in size. This is true in the sense that there is no significant increase in actinide concentration in the leachate (which may be due to colloids) over and above that expected due to actinide solubility. This does not rule out the possibility that the actinides are predominantly associated with colloids. However, there is higher  $\alpha$ -activity associated with colloids and particulates in the 0.1 -5.0 µm size range, particularly in ELT2. Given the relatively low colloid concentrations measured and the low activities in the solution fraction, this indicates a strong association between the principal  $\alpha$ -emitters in the tests (<sup>241</sup>Am and <sup>239/240</sup>Pu) and this particle size fraction.

These findings were supported by radiochemical and gross  $\alpha$ -analyses of fines fractions resuspended from the top surface of the upper cement layer and heater wells during dismantling of the tests. In particular, there was good correspondence in  $\alpha$ -activities for 5 µm filtered fractions of three of the four fines-containing leachates prepared over one year apart. This activity had previously been shown to be associated with particles in the 0.45 - 5.0 µm size range [30]. In the case of top-surface fines, following initial sedimentation of fast-settling material, a colloidal fraction appears to be left in dispersion that may not have changed significantly over the 15-month storage period. In ELT2, this was composed primarily of brucite (Mg(OH)<sub>2</sub>) particles about 300 nm in size. The  $\alpha$ -activities associated with the filter-retained colloid fractions of the top-surface fines after 15 months storage were 110 and 7300 Bq dm<sup>-3</sup> for ELT1 and ELT2, respectively.

During SEM/EDX analysis of slow-settling fines samples and colloidal fractions, no particles of uranium-, plutonium- or americium-containing phases were identified. These null results support the conclusion that the actinides are associated with the colloidal phases predominantly by sorption.

In addition to studies of colloid fractions, radiochemical analysis was also undertaken on faster settling (larger) fines material resuspended from the tests. It is noted that the  $\alpha$ -activity



associated with the filter-retained colloidal fractions from the fines samples (described above) are significantly less than the activities associated with fast-settling particulate material, which dominated the quantity of resuspended solid phases on a mass basis [30].

As part of the decommissioning study [30], the opportunity was taken also to sample and analyse the top cementitious layer in each test to obtain sorption information from a layer that had been in direct contact with the leachate with minimum contamination from solid wastes below. The activity associated with these materials could be considered as sorbed activity and be compared with leachate activities measured during the tests to estimate  $R_d$  values. It was found that the actinides were more concentrated in the top layer of the cements than their average concentrations in the tests. Estimated  $R_d$  values for <sup>241</sup>Am and <sup>239/240</sup>Pu in the ELTs were about 10<sup>7</sup> and  $3 \times 10^7$  cm<sup>3</sup>g<sup>-1</sup> respectively; values for U(VI) were about  $5 \times 10^5$  cm<sup>3</sup>g<sup>-1</sup>. These values were several orders of magnitude higher than typical values measured in batch sorption experiments on crushed cement materials. This was attributed to the presence of highly active fines in the cement samples analysed.

### 4.3.4 Organic colloids and the effects of organic complexants on sorption to colloids

A significant body of 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 PA were reviewed in 2004 by Heath and Williams [91].

In general, the presence of significant concentrations of complexants in solution that may compete with solid surfaces for the uptake of radioelements is found to reduce the effective sorption distribution coefficients for the solid. The magnitude of the effect depends on a number of factors including the mineralogy, the radioelement, the strength of complexation, etc. There may be some circumstances, in which sorption of organic complexants to a solid surface enhances the radioelement uptake onto the solid [196]. These types of effects may also arise on the surfaces of colloid particles as a result of competition or co-operative effects with organic complexants. However, to date all the work in this area has been undertaken on solid phases and the authors are not aware of any studies involving colloids (either near field or far field).

Although many studies have been reported in the literature of the interactions of natural humic substances with radioelements under geosphere conditions [e.g. 197,198], the authors are not aware of any published studies of the interactions of radioelements with organic macromolecular colloids of relevance to the near field of a cementitious repository.

Some work was undertaken on the Nirex programme in the late 1980s to study the effects of the four common types of superplasticisers on plutonium solubility at pH 12 [199]. Three of these materials are macro-polymers: naphthalene formaldehyde, sodium lignosulphonate and melamime formaldehyde. However, the plutonium solubilities were measured after ultrafiltering the solutions through 25,000 NMWCO filters and therefore, the measured solubilities represent the low molecular weight fractions. These fractions were found to increase plutonium solubility where the additive was present at high concentrations (0.5 to 1 wt%). However, solutions from the short-term (25-day) leaching of cured cement blocks containing 0.5 to 1 % of these materials gave no increase in plutonium solubility.

### 4.3.5 Additional data sources and approaches

Where insufficient data are available on near-field colloids, other approaches have been used to assess likely colloid  $R_d$  values and the likely impact of cement colloids in the near field. Here, three examples are examined.

### a) Comparison with natural far-field colloids

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 [200]. The distribution ratio for amorphous silica increased from  $\sim 10^2$  cm<sup>3</sup>g<sup>-1</sup> at pH 6 to  $\sim 10^5$  cm<sup>3</sup>g<sup>-1</sup> at pH 9. For quartz, the distribution ratio increased from  $\sim 5 \times 10^3$  cm<sup>3</sup>g<sup>-1</sup> at pH 5 to  $\sim 5 \times 10^5$  cm<sup>3</sup>g<sup>-1</sup> at pH 12. There was minimal difference in sorption between americium at  $10^{-10}$  mol dm<sup>-3</sup> and  $10^{-11}$  mol dm<sup>-3</sup>. Sorption onto amorphous silica decreased with increasing colloid concentration ( $10^3$  to  $10^2$  cm<sup>3</sup>g<sup>-1</sup>) 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<sup>-3</sup>. The sorption mechanisms for amorphous silica and quartz appeared to be different, but no mechanisms were discussed.

The sorption of technetium, caesium, strontium and promethium has been measured as a function of pH and particle size [201]. 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  $(1.2 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ at } 0.1 \text{ g dm}^{-3} \text{ to } \sim 500 \text{ cm}^3 \text{ g}^{-1} \text{ at } 10 \text{ g dm}^{-3})$ . 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.

Another study looked into the effect on the sorption onto granite of the presence of colloidal silica sol [202]. 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. For a near field backfill such as Nagra's M1 (Monokorn 1), which is 80% quartz, colloidal silica is expected to be present as the quartz reacts in the alkaline porewaters, so these data are generally directly applicable.

Work performed as part of the Nirex Research Programme on colloids was reviewed in 1998 [19]. A section is devoted to radionuclide - colloid interactions. The assumption was made that, for each radionuclide, sorption onto colloids should be a similar process to its sorption onto the rock (see also discussion in section 2). However, it would be expected that the sorption distribution coefficient for the colloids to be greater than that of the rock by a factor (F) that is related to their relative surface areas available for sorption (or the number of available sorption sites). Therefore, for each radionuclide:

$$K_{\rm nc} = F K_{\rm nr} \,. \tag{4.1}$$

where  $K_{nr}$  is the far-field sorption distribution coefficient for the rock.

In the absence of colloid-specific sorption data for the Sellafield area, information was taken from the literature for appropriate phases: silica, iron oxides and illite were identified as components of the colloid population isolated from the North Head Member, St Bees Sandstone at Sellafield. The  $K_{nc}$  values from laboratory studies are compared in Table 4.2 with 50 percentile far-field sorption distribution coefficient values for Sellafield, denoted  $K_{nr}(50\%)$ . The  $K_{nc}$  values are all larger than the corresponding rock  $K_{nr}(50\%)$  values and the ratios (scaling factors) have been calculated. The ratios 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), which is nearly an order of magnitude smaller than the particles isolated from the Sellafield groundwater. These comparisons suggested that a scaling factor of 300 was a reasonable estimate for calculating colloid sorption distribution coefficients for the Sellafield site.



## Table 4.2Experimental Distribution Coefficients for Radionuclide Sorption onto<br/>Colloidal Materials Derived from Natural Materials compared with Nirex 97<br/>Central Case Values for Sorption onto Rock

Colloid type & conditions	Element	Concentration (mol dm <sup>-3</sup> )	К <sub>пс</sub> [] (cm <sup>3</sup> g <sup>-1</sup> )	К <sub>nr</sub> (50%) <sup>а</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Scaling factor, <i>F</i> <sup>b</sup>
Grimsel colloids	Sr	1.6-16 × 10 <sup>-6</sup>	$6  imes 10^2$	2.7 × 10 <sup>1</sup>	$2.2 \times 10^{1}$
0.1 mg dm <sup>-3</sup> , clay & silica	Cs	7-140 × 10 <sup>-7</sup>	$2 \times 10^3$	$1.6  imes 10^2$	1.25 × 10 <sup>1</sup>
pH 9.6, P <sub>(CO2)</sub> 10-5.5 atm.	Am	$4 \times 10^{-10}$	$1 \times 10^{6}$	$3.2 \times 10^3$	$3.1  imes 10^2$
Zurzach colloids					
0.02 mg dm <sup>-3</sup> , clay and silica	Pb	2.8 × 10 <sup>-9</sup>	$5  imes 10^5$	$3.2  imes 10^3$	$1.6 \times 10^{2}$
pH 8.0, P <sub>(CO2)</sub> 10-3.5 atm	Ni	$2 \times 10^{-10}$	<10 <sup>4</sup>	$1.7 \times 10^2$	<6 × 10 <sup>1</sup>
SiO <sub>2</sub> (quartz) colloids					
1 mg dm <sup>-3</sup> , pH 8	Am	$8 \times 10^{-10}$	$2  imes 10^4$	$3.2 \times 10^3$	$6.25  imes 10^0$
SiO <sub>2</sub> (amorphous) colloids					
1 mg dm <sup>-3</sup> , pH 8, 20 nm size	Am	8 × 10 <sup>-10</sup>	$3  imes 10^6$	$3.2 \times 10^3$	$9.4  imes 10^2$
Montmorillonite colloids	Pb	2.8 × 10 <sup>-9</sup>	$5  imes 10^5$	$3.2  imes 10^3$	$1.6  imes 10^2$
рН 8	Ni	$2 \times 10^{-10}$	$5  imes 10^3$	$1.7 \times 10^2$	$2.9 \times 10^{1}$
	Am	8 × 10 <sup>-10</sup>	$3 \times 10^5$	$3.2 \times 10^3$	$9.4 \times 10^{1}$
Illite colloids					
рН 8	Am	$8 \times 10^{-10}$	$3  imes 10^5$	$3.2 \times 10^3$	$9.4 \times 10^{1}$

Notes:

а

b

The value chosen was the central case (50 percentile) value used in Nirex 97 [36]

The ratio of  $K_{nc}$  values from [55], to  $K_{nr}(50\%)$  values used in [36].

### b) Comparison with cement sorption data

In the Swiss programme, a not dissimilar scaling approach has been used to assess the likely impact of near-field colloids. Here, a highly permeable backfill (M1) was designed to ensure the release of gas generated in the near field and to ensure mechanical stability by filling voids in and around the waste containers. The M1 was considered a likely source of colloids and so experiments were carried out to assess colloid populations (details in section 2.2) which, at less than 0.1 mg dm<sup>-3</sup>, were somewhat lower than the NRVB-derived colloid populations. It was shown that the colloids produced in these experiments consisted of the same materials as the solid phase used (blocks of hardened cement paste, HCP) and so it was assumed that "...the chemical nature of the surface sites exposed both on HCP and cement-derived colloids are similar" [9]. Subsequently a calculation directly analogous to that performed for the Sellafield colloids, provided differences in radionuclide retardation on both materials based on their respective surface areas: ~50 m<sup>2</sup>g<sup>-1</sup> for HCP and 240-770 m<sup>2</sup>g<sup>-1</sup> for the colloids. The only difference here is that the solid phase is the cement, rather than the host rock at Sellafield.



The recent production of cement sorption data has provided a useful (if small) database on which to assess the approach further. For example, the interaction of Sr(II) and Ra(II) with calcium silicate hydrates (C-S-H) and fresh and degraded hardened cement pastes (HCP) has recently been investigated by batch sorption experiments [203, 204]. Synthetic C-S-H phases with varying CaO:SiO<sub>2</sub> (C:S) molar ratios, relevant to non-degraded and degraded HCP, were prepared in the absence of alkalis (Na(I), K(I)) and in an alkali-rich artificial cement pore water (ACW). The sorption kinetics, the effect of the solid to liquid ratio and the impact of the C:S molar ratio on the radionuclide uptake were investigated. In addition, sorption reversibility was tested using dilution tests.

The same model concept could be applied to interpret the immobilisation of Sr(II) and Ra(II) in these systems. Sr/Ra(II) sorption on C-S-H in the absence of alkalis could be interpreted in terms of a Sr/Ra<sup>2+</sup>-Ca<sup>2+</sup> cation exchange model. The Ra<sup>2+</sup>-Ca<sup>2+</sup> exchange selectivity coefficient, <sup>Ra</sup><sub>Ca</sub>K<sub>C</sub>, was determined to be 6 (±4) while that for Sr was 12 (±0.3). There are indications that, in the presence of alkalis, Ra(II) sorption by C-S-H phases can only be described with the help of an ion-exchange model involving Ra<sup>2+</sup>, Ca<sup>2+</sup> and the monovalent alkalis. For Sr(II), it was shown that both the sorption and co-precipitation tests resulted in Sr(II) distribution ratios which were similar in value, indicating that the same sites are involved in Sr(II) binding. A cation exchange model developed for C-S-H phases in the absence of alkalis was successfully applied to predict the sorption of both Sr(II) and Ra(II) on degraded HCP, assuming that the Ra(II) sorbs solely on the C-S-H fraction of the HCP and the Sr(II) uptake by C-S-H phases was described in terms of a Sr<sup>2+</sup>–Ca<sup>2+</sup> and alkali solution concentrations) and for Sr, an *R*<sub>d</sub> of 10<sup>2</sup> to 10<sup>3</sup> cm<sup>3</sup> g<sup>-1</sup> (absence of alkalis) was reported.

The behaviour of Ni has been studied in the same ACW solution as above and it was found that the concentration of dissolved Ni could not be modelled on the assumption that uptake is reversible, linear sorption [205]. Based on the experimental data, it is speculated that a solid-solution system may be controlling the Ni behaviour and a  $R_d$  of  $150 \pm 20 \text{ cm}^3 \text{ g}^{-1}$  was reported. On Ni loaded HCP samples, <sup>63</sup>Ni uptake could be interpreted as an isotopic exchange process with the stable Ni of the cement, but only a small portion of the stable Ni inventory is available for exchange.

### 4.4 Reversibility of sorption

Sorption and desorption rates of cation exchange reactions are generally considered to be identical within analytical uncertainty, generally because the cation exchange process is fast and reversible. However, sorption and desorption rates of surface complexation reactions may show some hysteresis. In the laboratory, most sorption processes occur within seconds to weeks but, in natural environments, it has been observed that the rate of desorption can take a hundred years. This may depend on many factors e.g.:

- diffusion into the structure of the solid phase;
- organic or inorganic coating 'sealing in' the sorbed radionuclide;
- incorporation in the solid phase during Oswald ripening

In particular, the significance of near-field colloids in the preferential transport of radionuclides is highly dependent on the irreversibility of the sorption process because, if radionuclides readily desorb when chemical changes occurs along the flowpath (e.g. when the pH fronts in the ADZ are encountered), colloids would have little effect on radionuclide migration from the near field.

Despite the importance of this process, little work appears to have been published on this aspect (e.g. see also comments in [9]). For example, although in [17] it was noted that *"Furthermore, nuclides released from a waste package would migrate through the mortar and bentonite in the engineered barrier by repeated sorption and desorption"*, no work on desorption



from cement or colloids was mentioned. However, it was noted that "Understanding sorption/desorption behaviour of nuclides on colloids and expansion of datasets" was a top priority for future research, which is currently ongoing in Japan at JAEA.

The most relevant information currently available are twofold: first, limited information on the reversibility of sorption on cement phases (but not colloids) and, second, data concerning sorption onto solid phases under far-field conditions. While neither of these datasets offer a direct insight into irreversibility of sorption on near-field colloids, in the absence of near-field results, the data are nevertheless useful.

### 4.4.1 Measurement of sorption reversibility on cements

In addition to the sorption studies on Sr and Ra discussed in Section 4.3, [203, 204] where the degree of irreversibility was examined. They noted that, in alkali-free solution, Sr(II) uptake was seen to be fully reversible, but only partly reversible in the ACW solution. This was interpreted to indicate that C-S-H phases exhibit equal affinities for  $Ca^{2+}$  and  $Sr^{2+}$ , but that the presence of high concentrations of alkalis interferes with this relationship in an, as yet, undefined manner. In the case of Ra(II), it was shown that uptake was fully reversible in both solutions.

### 4.4.2 Far-field colloids

The sorption/desorption of lead, bismuth and polonium onto montmorillonite has been reported [206]. 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 [207].

### 4.4.3 Natural analogue studies

Unfortunately, the studies cited above, along with all other, laboratory-based studies on reversibility/irreversibility of sorption, suffer from one major drawback: the temporal scale is too short to have any confidence in the results because kinetic effects can easily affect the results (see, for example, the discussion in [78] on Cs and U uptake on bentonite colloids). What is required is additional evidence from long-term, natural experiments – or natural analogues (see Box 2.1). The colloid natural analogue database is large but currently lacks one, unifying, overview of the relevance of both the focused colloid natural analogue literature and all the additional work from soil sciences, shallow aquifer and the chemo-toxic waste literature. Natural analogue evidence for the reversibility of radionuclide uptake on colloids is based mainly on uranium-series data. In particular, the measurement of uranium-series isotope distributions in groundwaters has been undertaken alongside colloid sampling programmes at a range of sites worldwide [e.g. 208, 209], and this has provided valuable data and insight into the uptake of these elements by natural colloids and their migration in natural systems.

A discussion of the collection of representative colloid samples from groundwater systems is beyond the scope of this review, except to say that it is essential that the methods used preserve the existing geochemical equilibrium in the groundwater/particulate/rock system under investigation. The avoidance of contamination (e.g. with drilling muds in boreholes) or artefact colloid formation (e.g. due to exposure to changes in atmosphere (i.e. pCO<sub>2</sub>), pH and/or redox conditions) during sampling and subsequent analysis are essential if representative data are to be obtained (see [138] for an overview).

In general, the volume of colloid sample required for physical and chemical characterisation is small  $(10^{1}-10^{2} \text{ dm}^{3})$ , but measurement of actinide activities by isotope dilution/alpha spectrometry techniques [210] or (for greater accuracy) thermal-ionisation mass spectrometry (TIMS) [211] requires much larger volumes  $(10^{2}-10^{3} \text{ dm}^{3})$ . The precision of colloid and actinide



activity analysis can be improved by concentrating the colloids contained in a large volume of groundwater, for example, by using tangential flow ultrafiltration (see also sub-section 2.2.6). The technique has been described extensively [e.g. 32,120]. Isotopic concentrations and activity ratios are measured for <sup>238</sup>U, <sup>234</sup>U, <sup>230</sup>Th, <sup>232</sup>Th and <sup>228</sup>Th. 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.

### a) Maqarin, Jordan

The above approach has been employed on near-field colloids only once, namely on those sampled in the Maqarin natural analogue site in Jordan [14]. Unfortunately, the amount of U associated with these near-field cementitious colloids was below the detection limit of the equipment then available (over a decade ago). Improvements in analytical techniques imply that it may be worth repeating the exercise now at the surviving site, the Western Springs.

Nevertheless, studies generally indicate that the <sup>234</sup>U/<sup>238</sup>U activity ratio of colloids is similar to that of the groundwater, indicating equilibrium between the two phases. In contrast, the <sup>230</sup>Th/<sup>234</sup>U activity ratios are often quite different, indicating disequilibrium. This may imply that the uptake of more strongly sorbed radionuclides such as thorium is not readily reversible. Two examples of this different behaviour can be examined in more detail at the Cigar Lake and Morro do Ferro ore bodies.

### b) Cigar Lake, Canada

A reasonably large, high quality dataset exists on colloids (and radiocolloids) in and around the ore body (see Figure 4.1) [212]. The original interpretation indicates that the colloid population is relatively low (~8 mg dm<sup>-3</sup>) for groundwaters. The isotopic signatures of the colloid-associated uranium and radium suggest that they have been taken up from the groundwater, rather than from the ore body, suggesting that the clay halo (Figure 4.2) has filtered any ore-derived colloids in the manner of the bentonite buffer in a HLW/SF repository (Figure 4.3).



### Figure 4.1 Location of the Cigar Lake uranium deposit, the second richest in the world (from [212])

### S N 0 m Waterbury - 40mGLACIAL OVERBURDEN lake PROTEROZOIC SANDSTONE Δ Δ quartz-cemented present-day groundwater cap flow altered sandstone clay-rich halo - 450m unconformity METAMORPHIC 0 100 m BASEMENT

Figure 4.2 Simplified cross-section of the Cigar Lake ore body, showing the clay halo which envelopes the ore and helps retain radionuclides (from [212])



Figure 4.3 Comparison of the Cigar Lake ore body and a design for a HLW repository; the original report [212] concluded that the clay-rich halo at Cigar Lake has filtered any colloids originating from the ore (Figure courtesy of Nagra)

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Nevertheless, this has not been proven unambiguously and, as there is some indication that the uranium may have been in association with the colloids for thousands of years, indicating both some degree of irreversible association of radionuclides with the colloids and very long-lived colloids, this may deserve re-analysis. Unfortunately, ongoing mining has presumably disturbed the site too much for further sampling and analysis, but the existing database may yield more information through a re-analysis of the raw data.

### c) Morro do Ferro, Brazil

At the site (Figure 4.4), it is possible to study colloid transport along the entire flow path, from the thorium-rare earth element (REE) ore source to surface springs. A series of sampling locations along the undisturbed groundwater flow path from the surface ore body at Morro do Ferro to the release point into surface waters at the bottom of the hill (Figure 4.5) allowed assumptions about the expected behaviour of colloids in this system to be tested. Measurements clearly showed that colloids containing significant concentrations of thorium and other relevant elements were present in the vicinity of the ore body but that, at locations downflow from this point, colloid signatures were completely different – reflecting local rock rather than the ore-influenced source water. Either the thorium had desorbed or, more likely, the colloids had been filtered out along the flow path.



### Figure 4.4 Location of the Morro do Ferro ore body, in the Poços de Caldas caldera, Brazil (from [213])

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Figure 4.5 The Morro do Ferro hill, one of the most naturally radioactive places on earth. The thorium-rare earth element ore body lies just below the crest of the hill (note spoil heap from the excavation drift which is at the base of the ore, just to the top left of the left hand tree). Image courtesy of Nagra

### d) Menzenschwand, Germany

Although not studied in as great detail as the previous two sites, the study of colloids at the Menzenschwand ore body in Germany's Black Forest produced a unique dataset which would appear to offer support to at least long distance transport of colloids. Here, the colloids in the groundwaters in and around the ore body contained Mg:Ti ratios and REE profiles which were more similar to the neighbouring gneiss (Felsberg, some 5 km away) than to the granite hosting the ore body [62]. However, the nature of these signatures is such that it is likely that they reflected the colloid 'core' rather than any sorbed material and so cannot be taken to support indications of irreversible uptake. Unfortunately, the uranium prospect was closed in the early 1990s and the mine allowed to flood, so re-sampling is not possible.

### e) The Nevada Test Site, US

This work [214] describes the transport of colloid-associated radionuclides (<sup>3</sup>H, <sup>60</sup>Co, <sup>137</sup>Cs, <sup>152,154,155</sup>Eu, <sup>239,240</sup>Pu) and uses the <sup>239,240</sup>Pu signature to identify the 'unique' source of the Pu colloids, some 1.3km from the sampling site. The vast majority (>90%) of all the isotopes studied (apart from <sup>3</sup>H) appear to be associated with colloids in this environment. This work purported to show that far field transport of Pu would be strongly influenced by colloids, especially as there was little sign of reversible uptake of the Pu. Unfortunately, the colloidal form of Pu was not defined and therefore the same caveats apply here as to distinguishing between 'core' isotopic and sorbed isotopic signatures and so cannot be taken to support indications of irreversible uptake of Pu on colloids.



These studies provide evidence that, despite the presence colloid-associated safety-relevant elements such as thorium in groundwaters, there is no clear, directly relevant evidence on near-field colloid radionuclide reversibility or irreversibility. However, several natural analogue sites exist where this could be addressed further and this is discussed in Section 7.

### 4.5 Summary of current understanding

As noted in the introduction, colloid sorption data of direct relevance to near-field colloids is rather sparse. This is generally justified by the fact that little data exist for near-field colloid populations and that which does exist has generally shown low populations, as would be expected for this high ionic strength environment. In addition, a lack of any mechanistic conceptual model of the likely evolution of the near field (discussed further in Section 7) is another reason against investing too much effort in colloid-association of radionuclide for the time being.

Where insufficient data are available on near-field colloids, other approaches have been used to assess likely colloid  $R_d$  values and the likely impact of cement colloids in the near field. However, once again, this has also been limited in extent and used little in repository PA. Although the NSARP approach for far-field colloids was used in the UK programme to scope potential colloid–associated sorption, this has not been repeated in a formal manner in any other PA to date. The basic premise is that for each radionuclide, sorption onto far-field colloids should be a similar process to sorption onto the host rock. However, it would be expected that the sorption distribution coefficient for the colloids would be greater than that of the rock by a factor (F) that is related to their relative surface areas available for sorption data much more simple as host rock sorption data are routinely produced for any site assessment and colloid surface areas can be routinely measured.

The simplicity of this approach is very attractive and certainly lends itself to relatively clear decisions on the likely relevance of radionuclide-associated colloids. However, what has not been done in either case is a detailed assessment of colloid surfaces to check that they are simply a scaled-up version of the near-field materials. This may well be the case in simple model systems, but may no longer hold in the true complexity of the near field.

Nevertheless, this approach has been extended in the Swiss programme in a preliminary assessment of the potential impact of the presence of colloids in the near field for the case of reversible sorption of radionuclides to both colloids and backfill material. In Figure 4.6, an increase in the sorption reduction factor ( $F_{red}$ ) indicates increased mobilisation of radionuclides in the cement porewater. This formulation indicates that the impact of colloids in the case of moderately sorbing radionuclides (i.e.  $R_d <~1 \text{ m}^3 \text{ kg}^{-1} \text{ or } 10^3 \text{ cm}^3 \text{ g}^{-1}$ , cf. NRVB-derived colloids above) is minimal up to colloid concentrations of about  $10^{-3} \text{ kg} \text{ m}^{-3} - \text{ i.e.}$  slightly greater than the level expected in the both the M1 backfill and the NRVB. It is only in the case where strongly sorbing radionuclides are present is there any appreciable impact at the likely colloid populations expected in the backfill, with  $F_{red}$ =2. It is worth noting, however, that these calculations also assume that sorption on both the HCP and the colloids are reversible [215].

This study assumes that the surface of the colloids is similar to that of the cement, so allowing the simple extrapolation of the cement data to the near-field colloids. However, as noted in section 2, this may not be the case and so it is questionable if it is possible to extend our limited understanding of cement sorption processes to this extent given, first, that a mechanistic understanding is still generally lacking and, second, given the likely highly complex nature of near-field colloids. In the first instance, recent studies have shown that a variety of uptake mechanisms are operating, for example:

• the incorporation of Cm(III) into the structure of CSH [216];



- a 'solution-like' coordination environment of Se(IV) and Se(VI) bound to a range of cement phases [217]; and
- Co(II) uptake on HCP as a cobalt hydroxide-like phase and/or Co-phylosilicates [218].

A basic understanding of the complexity of the near field has been provided by the few ELT experiments carried out to date. Although there are tantalising hints from the ELT experiments that there is indeed a significant radionuclide-colloid association (at least for the actinides), the under-definition of the colloidal and particulate phases means that it is difficult to make quantitative statements on likely colloid association. It is perhaps surprising that these types of experiments have not been repeated more than the few examples cited here and in Section 2 as they arguably offer the most realistic method of better assessing the true *in situ* conditions in a repository near field. However, if such complex, costly and long-term experiments are to be repeated, they should more accurately reflect the *in situ* conditions, including such aspects as solid:liquid ratios etc. It could be argued that such work should wait on the definitive design for the UK cementitious repository, but this overlooks the fact that carrying out an improved ELT experiment will provide the basic mechanistic understanding which will be required regardless of the design specifics.



Figure 4.6 Effect of colloids on the retardation of radionuclides in the near field of a Swiss cementitious repository for the realistic case [9]; F<sub>red</sub> denotes the sorption reduction factor in the presence of colloids; note that *R*<sub>d</sub> values are expressed in units of m<sup>3</sup>kg<sup>-1</sup>

If relevant data for cementitious colloids are scarce, then those for organic complexants are even rarer. However, given the current uncertainties over which cement admixtures will be used, this is not unreasonable and awaits firm decisions on repository design in the future.



Natural analogue evidence for the reversibility of radionuclide uptake on colloids is based mainly on uranium-series data and these cannot easily distinguish between uptake mechanisms on colloids (see discussions in [219, 220]). It also cannot yet differentiate between the composition of the 'core' of the colloid (which may be largely isolated from groundwater) and that of the colloid-water interface where uptake will be occurring, meaning that any signature is probably a mixed one from these two zones. However, recent improvements in analytical techniques suggest that it may now be possible to better differentiate between phases and so it would be worth looking at suitable sites to repeat this work (discussed further in Section 7).

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# 5 Migration of repository-derived colloids into the far field

### 5.1 Introduction

In this section, the potential for migration of repository-derived colloids into the far field will be considered. Although colloid transport in groundwater systems has been extensively studied, very little work has been undertaken to look specifically at the migration of repository-derived colloids either within the repository or into the far field. In major part, this is a result of the low concentrations of near-field colloids that have been measured in experiments to date (as outlined in Section 2) and the simplified near-field source term models used to date in PA (see Section 6 for further details).

Migration of repository-derived colloids into the far field first requires that near-field colloids are mobile in the near field. On the basis of the low colloid concentrations measured to date in colloid generation experiments and the destabilisation of simulant inorganic near-field and far-field colloids under the chemical conditions of the near field, the potential for colloid mobility in the near-field waters appears to be limited. Thus, it could be argued that migration of inorganic near-field colloids into the far field via the groundwater pathway is a non-issue.

There remain a number of uncertainties concerning near-field colloid populations and their stability that are of concern. These include:

- the potential presence in the near field of a small fraction of intrinsic radioelementcontaining colloids, and carrier colloids into which radioelements have been *ab*sorbed, that may be mobile;
- the potential generation of significant concentrations of organic waste-derived colloids in the repository that bind radioelements, e.g. due to the presence of superplasticisers;
- the potential generation of significant concentrations of organic compounds, or the migration of significant quantities of natural humic materials into the repository, that may act as surfactants and thus increase the stability of colloids under near-field conditions;
- the potential migration of colloids by transport processes other than advection and diffusion in groundwater, e.g. attachment to gas bubbles.

In the case of a cementitious repository, the situation is complicated by the migration of a chemically reactive plume, which will react will 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 (sub-section 1.4).

Two of the major uncertainties highlighted in the earlier review of colloids in the geosphere concerned [19]:

- The nature, stability and mobility of colloid populations in the ADZ; and
- The stability (or longevity) of near-field colloids on migration into the geosphere.

The latter concerns, primarily, the chemical stability of near-field colloids (principally cementderived colloids) under the changing chemical conditions experienced on migration into the lower pH conditions of the far field.


In the last Nirex assessment to include a treatment of colloid-facilitated transport, Nirex 97 [36], colloids were assumed to be mobile in the far field on the basis of available evidence (see discussion in [19]). Near-field colloids were assumed to be mobile within the near field but to dissolve and release their radionuclide burden to the groundwater on migration into the geosphere. This was considered to be a realistic assumption, given the metastability of inorganic colloidal particles when considering processes operating over geological timescales. Although the ADZ was mentioned in the Nirex 97 assessment, no attempt was made to model its effects in the assessment models.

Uncertainties remain concerning the nature, stability and mobility of colloid populations in the ADZ.

In the following sub-sections, these uncertainties will be discussed from a conceptual point of view drawing on previous discussion in reference [19] and current conceptual understanding of the evolution of the ADZ.

To date no serious attempt has been made to model transport processes in the near field of a cementitious geological repository as part of a PA. Conceptual models are available for near-field transport processes and model calculations have been made of transport processes within and from waste containers. However, there has been no attempt to incorporate colloid transport in the near field into such models. Given the range of scenarios highlighted above, it is appropriate to consider the transport and retardation processes that govern colloid migration in both the near and far field, and the transport pathways under consideration.

The situations in which either a cementitious repository is located in a clay formation (e.g. in Belgium, see Section 6.4) or a bentonite buffer is envisaged to surround the repository (e.g. Japan, see Section 6.5]) will not be considered here in detail. In these cases the host rock or a bentonite buffer is designed to act as a transport barrier to prevent groundwater flow into the repository, thereby ensuring that near-field transport is primarily diffusive [17]. These are also assumed to act as a colloid filter. In the case when either the low permeability host rock or the bentonite is fractured (e.g. by cementation following reaction with alkaline leachates and then fracturing by gas flow out of the repository), then they may also be assumed to behave like a fractured host rock (without a bentonite buffer). Work on the colloid barrier role of bentonite has been reviewed recently by Alexander and Neall [122]. Some work on diffusion of organic colloids through clay has been undertaken in Sweden [81,221,222].

#### 5.2 Transport processes in the near field

#### 5.2.1 Overview

Three processes can be identified by which particles can move in groundwater in both the near field and the geosphere:

- (a) 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 dissolved species. Particle transport may be slightly faster than solute or water flow as a result of size exclusion processes [223,224]. The hydrodynamic dispersion of colloids may be different from that of solutes if the groundwater flow paths of solutes and colloid are different [225].
- (b) 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. Not all the porosity of an aquifer 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 may diffuse into and out of these stagnant regions of the water volume provided that they are not excluded on the basis of size or charge.

(c) Sedimentation – under conditions of very low groundwater velocity, gravitational settling will act to retard the migration of inorganic (denser than water) particles. For spherical particles, the rate of settling is proportional to the square of the particle diameter and the difference in density between the particle and water according to Stokes Law. Thus the sedimentation rate increases significantly with particle size. For particles of colloidal size, sedimentation may be important under conditions that favour particle aggregation or growth, depending on the size, shape and density of the aggregates formed.

A number of additional transport processes can be envisaged by which near-field colloids could migrate within and potentially out of the repository. These processes arise as a result of the dissipation of energy that may result from physical and chemical processes that will occur within the near field over varying timescales. These include:

- flotation, by adhesion of particles to the surfaces of gas bubbles, which may form from the corrosion of metallic wastes (principally hydrogen) or from the degradation of organic materials present in the repository (methane, carbon dioxide, etc), and rise due to buoyancy;
- buoyancy driven flow of entrained particles in light non-aqueous phase liquids (LNAPLs) that may accumulate within a repository from both as-disposed oils and the degradation of organic materials; and
- buoyancy-driven ("piston") flow and induced movement of water associated with two phase flow processes arising from the accumulation and movement of gas or LNAPLs.

It is important to note that owing to the energy-release and flow rates potentially associated with the above processes, each could lead to increased particle release as a result of surface erosion. In addition, particulates of significantly larger size than colloids could potentially be mobilised. Partly for this reason, a detailed discussion of these processes is considered to be outside the scope of this report. However, both flotation and the movement of entrained colloids in a separate LNAPL phase depend on the surface properties of colloid particles to maintain adhesion or entrainment. Therefore, some further comments on these aspects of colloid behaviour are warranted here.

It should be noted that work on the generation and migration of gas and the potential formation, migration and impact of NAPLs on repository performance is ongoing as part of the NDA RWMD research programme.

Finally, it is noted here that convection, the turbulent flow of water arising from differences in buoyancy due to thermal gradients, is considered unlikely to arise in a repository after resaturation. However, it is considered likely that convection would have been an important transport process in the ELTs described in Section 2 that were maintained for 6 years at 50°C [30,102].

#### 5.2.2 Flotation

Flotation involves the adsorption of particles to the surfaces of gas bubbles. Flotation processes are very important commercially for the separation of minerals during ore processing. In general, these processes involve the use a variety of additives, including surfactants, to tailor the wetting properties of mineral surfaces to control their adhesion (or not) to gas bubbles. A review of the principles is given in a number of standard texts [e.g. 226,227].

A limited number of minerals have what is known as 'native flotability', which means that they are flotable in water without the aid of surfactants. These minerals include graphite, coals,



sulphur, talc and pyrophyllite, which have in common a non-ionic surface character [228]. Experimental studies in the US 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 [24].

Hydrogen and other gases will be generated within a repository as a result of processes such as corrosion of metals or microbial activity and there is a likelihood that bubbles of gas will form and migrate in the near field [229]. Therefore there is the potential for particle transport by flotation to arise within a repository. This may occur spontaneously for finely-divided particles of natively floatable materials present in the wasteform, such as graphite, that come into contact with gas bubbles.

In addition, surfactants will be present in waste oils disposed to a repository and may be generated from the degradation of organic waste materials [230]. They may also arise from biological processes if viable microbial populations are present. Such surfactants may dissolve into the porewater and adsorb at gas-liquid and solid-liquid interfaces. Surfactants that sorb onto the surfaces of hydrophilic particles (such as metal oxides or CSH gels) may promote their adhesion to gas bubbles. For flotation to occur, suitable surfactants that will sorb onto hydrophilic mineral surfaces under the high pH conditions of the near-field are required and these need to be present at sufficient concentrations in the porewater to alter the wettability of the mineral. Clearly, there is greater uncertainty about the potential operation of such processes in the near field.

The point has been made previously in Section 3.8, that currently there is little information available concerning the presence and formation of potential surfactants within a UK ILW repository, although the degradation of organic materials is an area of ongoing research under the NDA RWMD programme. Given the uncertainties surrounding these processes, an assessment of whether flotation may be a significant process in the near field is not yet appropriate. In reality, particle transport by flotation will be of secondary importance to repository safety compared to gas migration.

#### 5.2.3 Colloid entrainment in NAPLs

For the process of colloid entrainment and transport with NAPLs, two cases can be considered: colloid adsorption at the water-NAPLs interface, akin to flotation; and partitioning, i.e. dispersion, of the particles into the non-aqueous liquid phase. For either of these processes to occur, the particles must possess or acquire a degree of hydrophobic, non-ionic character. The requirement is similar to that required for flotation.

Both of the above cases are important technologically. Important types of non-aqueous dispersions of inorganic particles include drilling fluids, calcium carbonate additives in engine oils and mineral pigments in oil-based paints. A feature of these systems is that they contain significant concentrations of surfactants, which are added to stabilise the inorganic colloid components of the dispersion.

Adsorption of solid particles at the oil-water interface is important for the stabilisation of emulsions and is responsible for unwanted water-in-oil emulsions that can be produced during crude oil production. Such emulsions, which are stabilised by the presence of solid particles that are much smaller than the drops of immiscible liquid, are examples of Pickering emulsions; their formation has been widely studied [231]. In the case of crude oil Pickering emulsions, stabilisation is due to the adsorption of asphaltenes (heavy, polar fraction of crude oil) onto clay minerals [232]. In general, adsorption of the surfactant onto the particles alters the wetting characteristics of the particles so that they are not preferentially wetted by either of the liquid phases, that is, they become what is known as intermediate-wet. Adsorption of the particles at the oil-liquid interface minimises the interfacial energy. Coalescence of the water drops in the emulsion requires the removal of the stabilising particles from the interface and their dispersion in the continuous oid phase, which requires significant energy input.



There are also examples in the literature in which particle stabilisation of emulsions has been achieved without requiring a surfactant, for example with layered double hydroxide minerals [233].

The dispersion of particles by NAPLs in geological materials has been reported in the literature. In a study of the impact of additives in a chlorinated hydrocarbon dense NAPL (DNAPL) on the wettability of sandstone, Harrold *et al.* [234] found that the DNAPL draining from sandstone cores on water imbibition had changed colour from clear to rust brown. This was due to the removal of iron oxide particles from the mineral surfaces of the cores. The mechanism of iron oxide removal was not investigated, but it was postulated that the particles had been removed by interactions with the octadecylamine additive used in the tests, which was present in the DNAPL at concentrations ranging from 0.01 to 0.1% by weight. Despite adsorption of the additive to the sandstone cores, which was expected to lead to an increase in the water/DNAPL interfacial tension (IFT), a significant reduction in the IFT was measured. Further tests in which mixtures of water, DNAPL and amine were contacted with powdered goethite demonstrated that the IFT was depressed by the presence of iron oxide particles. Furthermore it was found that Pickering emulsions of DNAPL in water could be readily formed in the presence of goethite and octadecylamine.

A similar drop in IFT for hexadecane/water systems in the presence of dodecylamine and kaolinite particles attributable to kaolinite adsorption on the water side of the NAPL/water interface has been reported by Wang *et al.* [235].

In all of the above cases, suitable surfactants were present at significant concentrations, generally 0.01% or above within the experimental systems. There is considerable uncertainty as to whether potential surfactants would be present in sufficient concentrations within the near field to stabilise hydrophilic particles. This is in addition to the considerable uncertainties concerning the potential impact of LNAPLs on repository performance. There is a significant uncertainty about the rate at which LNAPLs may be generated from wasteform degradation and whether significant volumes of free LNAPLs phase will accumulate within and migrate out of a repository before they are dissolved or consumed by microbial activity.

Therefore an in-depth assessment of the potential for colloid transport by entrainment in LNAPLs is not appropriate at present. Work to scope the potential impact of LNAPLs is currently in progress on the NDA RWMD programme. Nevertheless, the potential for entrained particle transport with mobile LNAPLs, particularly of non-ionic materials, should be recognised. The results of Harrold *et al.* [234] suggest that there is potential for the suspension of particulate deposits by contact with LNAPLs

#### 5.3 Transport pathways in the near field

The groundwater pathway models applied in Nirex assessments have considered a deep repository excavated in a low-permeability fractured hard rock overlain by a sedimentary cover. The predominant pathways for colloid transport through low permeability fractured rocks (such the Borrowdale Volcanics Group at Sellafield) are considered to be fractures and fracture networks (Type I and Type II features), where fracture dimensions are large compared to the size of colloidal particles. However, the overlying sedimentary layers are assumed to be more porous and contain fewer fractures; groundwater flow and colloid transport may occur through the porous medium.

Detailed conceptual models for transport in the near field of a deep cementitious repository that account for groundwater flow and the advective and diffusive transport of radioelements (in addition to near-field chemistry), could be readily developed. There are clear conceptual similarities between the mechanisms and pathways for migration in the near field and those that operate in the far field, although the nature of the source input may be conceptualised rather

differently (diffusion/advection from a waste canister as opposed to advection into a flowing fracture).

The near field contains porous backfill which may fracture and these fractures plus voids in the waste packages may provide the predominant flow paths through the waste stacks. Some flow may also arise through the matrix porosity of the backfill and material may be leached from waste packages as a result of flow or diffusion.

Thus, a combination of fracture flow and porous medium transport may need to be addressed if consideration is given to the inclusion of colloids in near-field transport models.

#### 5.3.1 **Porous medium transport**

The advective transport of colloidal particles through porous media has been studied extensively in the context of deep bed filtration (see for example [236]). Three mechanisms of particle filtration by a porous matrix are related to the relative physical dimensions of the particles,  $d_c$  to the media or pore throat ( $d_t$ ) sizes:

- i) surface filtration (applicable where  $d_c > d_t$ );
- ii) straining filtration or pore throat bridging (where  $d_t > d_c > -1/5 d_t$ );
- iii) physico-chemical surface attachment (sorption) (where  $d_c < 1/5 d_t$ ).

Each of these mechanisms will act to restrict colloid penetration into a porous rock matrix.

Account can be taken of mechanisms i) and ii) based on physical data where available. Mechanism iii) is dependent on the balance of forces acting between a colloid particle and a surface (and for inorganic particles, the understanding of this process is based on application of the DLVO theory, as outlined in Section 3). The same mechanism will operate on the surface of fractures to immobilise or retard colloid migration.

Surface filtration processes may operate at the interface between near-field materials with different porosity or permeability characteristics or where the flow regime changes from fracture flow to matrix flow. Particles that may have been advected through a crack or fracture may be excluded from the porous medium due to their size, leading to the formation of a surface or interfacial filter-cake at the medium surface. In the case of cementitious repositories surrounded by a bentonite buffer or low-permeability mudrock, surface filtration is the mechanism by which colloids are excluded by the buffer barrier.

Straining filtration refers to filtration that occurs within the medium 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 [237]. This can lead to the formation of an internal filter-cake.

Finally, it is noted that channelling of mobile colloid particles (that is exclusion from parts of the matrix) could occur in a porous medium owing to variations in permeability through the matrix. It is therefore, possible for unretarded particles to travel faster than the average flow velocity (see below).

#### 5.3.2 Fractured medium transport

Where the principal water flow occurs through fractures or cracks in the backfill, waste packages or between the two, it is anticipated that colloid migration will be constrained largely to those fractures as a result of:

- i) size exclusion from the matrix of the wasteform or backfill;
- ii) electrostatic exclusion from the matrix of the wasteform or backfill.

As noted above, penetration of the matrix porosity by colloidal particles will depend on the pore throat size and the size distribution of the colloid population. Diffusion of colloids into the backfill matrix and possible surface attachment therein, would act as a retardation mechanism for colloid transport in these circumstances.

Flow through a fracture usually exhibits Poiseuille flow, that is the fluid velocity is zero at the fracture wall and reaches a maximum value in the centre of the fracture. The velocity profile, generally, is parabolic and the flow velocity at the centre may be up to 50% greater than the average value. Owing to their size and excluded volume effects, colloidal particles tend to travel in the faster flowing portions of the fracture, and may migrate at speeds faster than the average flow velocity. This well-documented phenomenon is referred to as hydrodynamic chromatography [223,224].

#### 5.3.3 Implications for near-field colloid mobility

Owing to filtration and sedimentation effects [238], 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. Similarly, under low flow conditions, it is expected that colloidal particles rather than larger particulates will potentially be mobile in near-field waters (although mobility will be limited by stability considerations).

At a physical level, the potential mobility of colloidal particles through the repository will be controlled by the aperture dimensions of the flow paths. In cracks and voids, where the dimensions of flowing features may lie between a few microns to centimetres, the predominant mechanism for colloid particle capture will be physico-chemical attachment and mobility may be controlled by the particle-surface interactions in addition to particle aggregation. Straining filtration could occur at a constriction in a fracture and, if there is significant flow into an adjacent porous matrix, then surface filtration may occur at the interface. For transport within the backfill, both straining filtration and surface attachment may be important retention mechanisms.

Particles that are filtered mechanically during flow through the near field may be redispersed if there is a change in the flow field acting on the particle. Particles that are sorbed to the rock may be released by thermal motion [239], a change in the flow field or by the collision of a particle in the fluid. In general, the rate of desorption of particles by thermal motion is controlled by an energy barrier that depends on and is very sensitive to the solution chemistry (e.g. pH, ionic strength, ion valency). Under conditions where the energy barrier is low (up to a few kT), and in the absence of other processes that may lead to an increase in the colloid-surface interactions, particle attachment to the surface may be considered a reversible process. However, if the energy barrier is sufficiently high, the rate of colloid release may become negligible and colloid attachment may appear to be effectively irreversible under the prevailing conditions. However, particles that are deposited under one set of conditions may be released by a change in chemical conditions, e.g. a reduction of electrolyte concentration or a change in pH [239]. While the near-field chemical conditions as a whole are expected to remain at high pH and high calcium concentration for a very long time, local variations in conditions are expected to occur in niche environments, such as in supercompacted PCM waste containers for example (see also comments in Section 7).



#### 5.3.4 Implications for high-energy transport processes

The above discussion has focused on colloid transport and mobility within the near field by the groundwater pathway. Clearly the transport pathways available will constrain the flow characteristics of other processes that may cause particle movement in a repository. It should be noted that the transport pathways followed by migrating gas and LNAPLs phases are likely to diverge from those followed by the groundwater owing to buoyancy effects. This will depend on the geological characteristics of the site and the hydrostatic gradients in and around the repository. A more detailed discussion of gas or LNAPLs pathways and mechanisms of particle retardation associated with gas or LNAPLs transport processes is beyond the scope of this report.

#### 5.4 **Conceptual model of ADZ development – implications for colloids**

As noted in Section 5.1 above, in the Nirex 97 assessment near-field colloids were assumed to be mobile within the near field but to dissolve and release their radionuclide burden to the groundwater on migration into the geosphere. The basis for this argument was that on moving from the high pH cementitious environment of the near field to the near-neutral conditions in the undisturbed geosphere (i.e. beyond the ADZ), the equilibrium that may exist in the near field between colloid formation and loss would be broken and the near-field colloids will be subjected to evolving local conditions through the ADZ [19]. Therefore, it was argued that in the geosphere, near-field colloids would be lost due to dissolution processes or aggregation and sedimentation, and that colloids of a different composition may be formed in the ADZ. It was proposed that individual near-field colloids have finite lifetimes in the geosphere. This argument is considered to be appropriate for all inorganic near-field derived colloids. However, the timescales of these colloid-loss processes and the resulting lifetimes and mobilities of near-field colloids in the geosphere are uncertain.

Understanding of processes in the ADZ has improved significantly since Nirex 97. For example, a simple generic conceptual model of the evolution of the host rock within the ADZ as alkaline leachates migrate away from the cementitious repository was developed as part of the Maqarin natural analogue [240] and is shown in Figure 5.1. This conceptual model for the ADZ provides a framework to start thinking in more detail about colloid formation and loss under the non-steady state conditions in this part of the geosphere.

Briefly summarised, the model assumes that the leachates are pushed from the cement (following mixing of groundwaters with the cement pore waters) due to the flow of groundwater into the cement further upstream [241,242]. At the cement/host rock interface (the proximal part of the plume), the alkaline leachates have not yet reacted with the host rock and so have a high pH and high concentrations of sodium, potassium and calcium, reflecting the cement porewater chemistry. As the plume reacts with the host rock, the pH falls, as do the sodium, potassium and calcium concentrations in the groundwater, while the concentrations of aluminium and silicon rise fractionally. Beyond the distal edge of the plume, in the, as yet, pristine host rock, the groundwater pH is near neutral, the sodium, potassium and calcium concentrations are lower and the concentrations of both aluminium and silicon are higher than in the plume waters.

This pattern has consequences for the secondary mineralogy and colloid production: CSH phases will be found in the fractured rock/porous media in the proximal part of the plume (through which the plume has been migrating), reflecting the fact that the host rock is reacting with leachate that was equilibrated initially with the CSH phases that make up the cement. As this process of reaction is occurring, colloids may be formed in the saturated (to supersaturated) solutions. As the leachate moves downstream and interacts with the aluminosilicates in the host rock (and the host rock groundwater and porewater), the aluminium concentration increases, precipitating CASH phases – and, once again, colloids may be formed. At the distal edge of the plume, the leachate has reacted with an even larger volume of host rock and eventually precipitates minerals such as zeolites as the aluminium concentration in the groundwater



becomes high enough and the pH low enough [243]. Although not studied in detail, it is assumed that any colloids produced in and around these reaction fronts will reflect the mineral zones produced. In other words, the passage of the leachates through the host rock will produce colloids which essentially reflect the composition of the 'true' near-field colloids. How stable they will be is not known, but it is assumed that they will begin reacting as soon as they pass out of their stability field.



Figure 5.1 Conceptual model of the alkaline plume evolution (from [240])



If it is assumed that the plume continues to migrate, then the zeolite zone produced by the distal part of the plume will gradually be exposed to leachate of higher pH, higher sodium, potassium and calcium concentrations and lower aluminium and silicon concentrations (i.e. the middle part of the plume). This will induce some re-dissolution of the zeolite phases and replacement by CASH phases potentially with associated production of colloids.

As plume migration continues, the mixed zeolite/CASH zone will be then contacted by higher pH waters (the proximal part of the plume), inducing further re-dissolution of the zeolite/CASH phases and replacement by CSH phases (once again, potentially with associated production of colloids). These complex mineral mixtures have been observed in places at the advective-flow dominated fractured host rock site at Maqarin, Jordan (see [121] for details).

Potentially, at least, the constant production and destruction of colloids in the ADZ could be associated with radionuclide uptake. Unfortunately, the appropriate zones of interaction at the Maqarin site were not accessed so no evaluation of these complex colloid mixes has been carried out (although this could be possible at the surviving site, the Western springs).

#### 5.5 Modelling colloid transport in the near field and ADZ

No requirement to model colloid transport via the groundwater pathway in the near field or the ADZ of a cementitious repository can be foreseen in the immediate future. Therefore, no attempt has been made to review recent developments in far-field colloid transport modelling as part of this study. This is a mature subject, with a significant body of literature. A wide range of colloid transport and coupled colloid-solute transport models have been developed dating from the 1980s onwards. Work undertaken on the Nirex programme in this area up to 1998 is reviewed in reference [19].

As far as the ADZ is concerned, there is a clear need to develop thermodynamic and reactive transport models to interpret laboratory data on the chemistry of the ADZ, which is being obtained on a number of experimental programmes worldwide. Such work will enable the development of conceptual models for solute transport through this zone. Until solute transport models have been developed, however, treatment of colloids in the ADZ would seem premature.

At present, there is a lack of experimental data on potential colloid generation and removal processes under the chemical conditions in the ADZ, to underpin the development of conceptual models for colloid behaviour in this zone. It should be recognised, however, that 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 conditions through the ADZ.

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### 6 Treatment of near-field colloids in PA for cementitious repositories

#### 6.1 Introduction

In this Section, the approaches adopted to treat near-field colloids in several recent performance assessments of cementitious repositories, chosen to reflect a range of EBS designs, host rocks and waste types, will be compared with that taken previously in the UK programme in the Nirex 97 assessment [36]. The focus will be on near-field processes (but will include the far field where this is relevant to the way near-field colloids are treated) and will include:

- the treatment of near-field colloid migration in PA
- potential implications/impacts of near-field colloids
- where data are available, the impact of near-field colloids in source term models, including estimation of radionuclide sorption distribution coefficients for colloids
- a brief comparison with the treatment of near-field colloids in other types of repositories (e.g. HLW/SF with bentonite buffer)

The PAs to be examined are listed in Table 6.1 and, after examining the treatment of near-field colloids in each PA in Sections 6.2 to 6.6, the information will be summarised in Section 6.7.

It should be noted that these assessments differed in their objectives and the levels of detail in which colloids (in general) were treated vary significantly. The Nirex 97 and Wellenberg [83] assessments were major PAs undertaken in the mid-1990s in which the potential impact of colloids was treated specifically in reference and/or variant calculations. The more recent SAFIR-2 (2001) [244] and TRU-2 (2007) [17] assessments are state-of-the-art reports on radioactive waste disposal rather than detailed PAs; in SAFIR-2 the discussion of colloids is limited to FEP analysis. This was also the case in the Project Opalinus Clay assessment (2003) [79], in which most of the near-field colloid FEPs were screened out at an early stage of the assessment process.

In reading these PAs, it rapidly becomes clear that in only a very few cases are near-field colloids deemed significant. Indeed, in many cases there is little effort made to separate the impact of near-field and far-field colloids, the results sometimes being rather confusingly lumped together in the text, if not in the treatment. The exception to this is the Nirex 97 assessment in which near- and far-field colloids were treated explicitly and independently. For this reason, the mathematical treatment of near-field colloids in Nirex 97 will be discussed in some detail. The Nirex 97 near-field models were also used in the most recent published Nirex generic PA, GPA03 [245] (although colloids were omitted). However, it is understood that the near-field model is under development for future NDA RWMD assessments.

Note that each assessment uses slightly different terminology which can cause confusion, but it was decided to stick with the original terms for reasons of authenticity and ease of later reference to the original documentation.

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Performance assessment	Organisation	Waste type and EBS design	Host rock description
Nirex 97 [36]	Nirex (NDA), UK	L/ILW isolated in cement, emplaced in vaults with cementitious backfill	Borrowdale Volcanic Group, a fractured, heavily weathered volcanic sequence overlain by higher permeability sediments
Wellenberg [83]	Nagra, Switzerland	As above, but with horizontal access to an 'in-mountain' repository	Palfris Formation of the Valenginian Marl, a fractured and heavily tectonised clayey limestone
SAFIR-II [244]	ONDRAF/NIRAS, Belgium	Long-lived ILW in vaults backfilled with cementitious material co-located with HLW/SF in vaults with clay (+/- sand/graphite) backfill and concrete liners	Boom Clay, a plastic clay overlain by higher permeability sediments
TRU-II [17]	JAEA/FEPC, Japan	As above, but with possibility of bentonite layer between EBS and far field. Co-location (with HLW) also considered	Generic, but uses the range described in the H12 PA, i.e. indurated and unindurated Neogene sediments and fractured crystalline
Project Opalinus Clay [79]	Nagra, Switzerland	Long-lived ILW isolated in cement, emplaced in vaults with cementitious backfill, co-located with a HLW/SF/MOX repository	Opalinus Clay, an indurated claystone, over- and underlain by higher permeability sediments

#### Table 6.1 Overview of the PAs considered in this Section

#### 6.2 Nirex 97 (UK)

#### 6.2.1 Disposal concept and site

In this assessment [36], geological disposal for radioactive waste, using a multi-barrier containment system, was considered. Vaults would be excavated at depth in a stable geological environment. Wastes, packaged in steel or concrete containers, would be placed in excavated vaults, which would then be backfilled with a high-permeability cement-based material (the NRVB) [92]. It was assumed that the host formation for the potential repository vaults at Sellafield (NW England) comprised rocks of the 460 Ma Borrowdale Volcanic Group (BVG) of the Lake District Massif. The BVG, a low-permeability, fractured hard rock, is overlain



by a sequence of sedimentary formations including the relatively more permeable rocks of the Sherwood Sandstone Group. Figure 6.1 provides schematic views of the repository vault design.

As noted in [36], the assessment was not based on a formal scenario analysis as would be the case in a comprehensive assessment, such as for the Wellenberg site (see sub-section 6.3). As such, there has not been a full treatment of the FEPs that might impact on repository performance. Here, as in Nirex 95 [246], the assessment approach was to develop scenarios based upon a number of potential routes by which a repository-derived radiological dose could be received. Nirex 97 considered both groundwater and gas pathways. Suites of probabilistic and deterministic calculations were undertaken for the groundwater pathway to investigate different scenarios and variant cases; deterministic sensitivity studies were undertaken for the gas pathway.



#### Figure 6.1 Cavern vault cross sections (from [36])

#### 6.2.2 Treatment of colloids in the near field

#### a) Conceptual models

In Nirex 97, the release of radionuclides from the repository vaults via the groundwater pathway was calculated using a solubility-limited source term (SLST) model [247]. Each vault was treated as a homogeneous well-mixed system. The effects of radionuclide transport within the near field and containment of the waste within waste packages were not therefore considered in the model. The radionuclide flux to the geosphere was determined by solubility limits and the extent of sorption onto the backfill. It was assumed that sorption of dissolved radionuclides onto near-field materials (primarily the backfill) is a linear, reversible, equilibrium process. This was based on the assumption that there would be a sufficiently large number of sorption sites available for sorption that competition for sorption sites between different radionuclides and other components of the near-field porewater would be unimportant [36].

As a basis for the treatment of the effects of near-field colloids, the following general assumptions were made:

- colloids are uniformly distributed throughout the flowing porosity in the waste and backfill with temporally and spatially constant concentration;
- colloids are excluded from a portion of the backfill porosity owing to size or charge exclusion effects;
- colloids do not interact (sorb) with the backfill;
- sorption of radionuclides onto colloids is reversible and can be described by a linear sorption isotherm as for sorption onto the backfill .

Note that the third bullet point was a cautious assumption, in the absence of available information concerning the interactions of near-field colloids with the backfill. However, a range of colloid-rock surface interaction behaviours were noted for far-field colloids [21,34].

Owing to considerable uncertainties concerning colloid stability and colloid sorption onto surfaces in the near field and lack of available information concerning processes that may lead to irreversible incorporation of radionuclides into colloids, the case of irreversible sorption of radionuclides to colloids was not considered in the assessment calculations (in both near and far fields). In fact, the treatment of near-field colloids in the source term models in Nirex 97 requires no assumptions to be made concerning the reversibility of radionuclide sorption to colloids within the near-field. The effects of transport processes through the near field that potentially would discriminate between the effects of reversible and irreversible-type sorption processes to mobile colloids, were not included in the models. Therefore, the near-field models provided a highly cautious treatment of near-field releases.

For the case of reversible sorption of radionuclides onto colloids, the effect of colloids on the source term could be calculated without altering the SLST model by introducing effective parameters that take account of the estimated loading of near-field colloids with each radionuclide. The effect of radionuclide sorption onto colloids is, potentially, to increase the effective near-field solubility limits and decrease the effective near-field sorption distribution coefficients for each radionuclide in each type of vault. The mathematical basis for this approach, which is outlined in a separate report [35], is outlined in the following sub-sections.

In the Nirex 97 near-field model, the effect of complexation by organic degradation products from the waste on radionuclide sorption and solubility was accounted for by sorption reduction factors and solubility enhancement factors. This treatment was based on the experimental observations that organic (principally cellulosic) degradation products may form complexes with certain radionuclides and that these complexes have enhanced solubility compared to uncomplexed dissolved species [248,249]. In addition, although organic complexants bearing radionuclides may bind onto solid surfaces, in general, the net effect of organic complexation has been found to be a reduction of the sorption distribution coefficients for certain radionuclides onto the backfill.

For Nirex 97, the effects of the exclusion of anions from parts of the porewater volume were incorporated into the SLST model and also into the geosphere models. Colloidal particles are expected to be negatively charged at the high pH of the near-field porewater and may also be excluded from regions of the backfill porosity due to charge repulsion effects. Furthermore, owing to their larger size, colloids may be physically unable to pass through the finest pore throats in the backfill. Therefore, the treatment of exclusion of colloids was incorporated into the mathematical treatment. However, as the effect on the source term was found to be negligible for all of the radionuclides considered, the treatment of colloid exclusion has been omitted from the discussion below.

#### b) Effective pore water concentration in the presence of colloids

The total amount of radionuclide type *i* dissolved in the near-field porewater in a given vault is given by  $\varphi_V V C_i$ , where  $\varphi_V$  is the average porosity of the vault of volume V and  $C_i$  is the



radionuclide porewater concentration. If the aqueous concentration of element *i* is not solubility limited, its total inventory,  $M_i$ , is assumed to be distributed in the near-field porewater and on the repository materials. In this situation, the porewater concentration is given by:

$$C_i = M_i / \alpha_i \gamma^i V \quad , \tag{6.1}$$

where  $\alpha_i$  is the effective capacity factor for the vault for element *i* given by the sum of the capacities of the porewater volume, the sorption capacity of the backfill and the sorption capacity of colloids entrained in the porewater, which is given by:

$$\alpha_i = \varphi_v (1 + m_c c_c \omega_c^i K_{nc}^i) + \beta \omega_R^i \rho K_d^i \quad .$$
(6.2)

The first term on the right-hand side of equation (6.2) represents the porewater capacity augmented by the sorption capacity of colloidal particles dispersed in the porewater solution. Here  $m_{\rm C}$  is the mass of a colloidal particle,  $c_{\rm c}$  is the near-field colloid number concentration,  $K^{i}_{\rm nC}$  is the sorption distribution coefficient for sorption for radionuclide type *i* onto near-field colloids and  $\omega^{j}_{\rm C}$  is the organic sorption reduction factor for sorption onto colloids.

The second term of equation (6.2) represents the sorption capacity of repository materials, taken to be dominated by the backfill. Here  $\beta$  is the fraction of the vault volume occupied by the backfill,  $\rho$  is its average dry density,  $K_d^i$  is the average equilibrium distribution coefficient for the sorption of element *i* onto the backfill and  $\omega^i_R$  is the sorption reduction factor due to organic complexants for sorption onto near-field materials.

The term  $\gamma^i$  in equation (6.1) is an exclusion factor for each radionuclide, which represents the fraction of porosity accessible to that radionuclide accounting for charge exclusion effects and is less than or equal to unity.

Assuming that all porewater leaving the repository carries a colloid concentration  $c_c$ , the effective solution concentration of radioelement *i* in the porewater leaving the repository (i.e. dissolved plus colloid-borne concentrations) can be expressed as<sup>9</sup>:

$$C_{\rm eff} = \frac{M_i}{(\varphi_{\rm v} + \beta \omega_{\rm R}^i \rho K_{\rm d, eff}^i) \gamma^i V} .$$
(6.3)

where

$$K_{\rm d,eff}^{i} = \frac{K_{\rm d}^{i}}{(1 + m_{\rm c}c_{\rm c}\omega_{\rm c}^{i}K_{\rm nc}^{i})}$$
 (6.4)

 $K^{i}_{d,eff}$  represents an effective sorption coefficient for the backfill in the presence of radionuclide sorbing colloids entrained in the near-field porewater. Note that as defined,  $K^{i}_{d,eff}$  accounts for the effect of organic complexants on radionuclide sorption to colloids but does not account for

<sup>&</sup>lt;sup>9</sup> Equation (6.3) also includes a term to account for the possible reduction in porewater volume accessible to colloids owing to size and charge exclusion effects. This factor, which is applied to the porosity term in the denominator only, has been omitted here because it was found to have negligible effect on the source term for all radionuclide considered in the assessment.

the effect of organic complexants on radionuclide sorption to the backfill. The sorption reduction factor,  $\omega^{i}_{R}$ , is applied to  $K^{i}_{d.eff}$  separately according to equation (6.3).

#### c) Effective near-field solubility limits in the presence of colloids

In the SLST model, the porewater concentration of radionuclide type *i*, was compared with the solubility limit to test whether the radionuclide concentration was solubility limited. In the presence of organic complexants, the solubility of the radionuclide may be enhanced by complexation. Therefore, the solubility limit in true solution is given by:

$$C_{\rm SL}^i = C_{\rm S}^i \xi^i \,, \tag{6.5}$$

where  $C_s^i$  is the near-field solubility limit for a given radionuclide in the absence of organic complexants (and in the absence of colloids) and  $\xi^i$  ( $\geq 1$ ) is the near-field solubility enhancement factor accounting for complexation.

Clearly, the effective solubility limit may be enhanced by radionuclide sorption onto colloids. Therefore, the effective solution concentration calculated using equation (6.3), was compared with an effective near-field solubility limit that accounts for colloids, given by:

$$C_{\rm SL,ef}^{i} = C_{\rm sc}^{i} \xi^{i} \,. \tag{6.6}$$

where

$$C_{\rm sc}^i = C_{\rm s}^i \left( 1 + m_{\rm c} c_{\rm c} \omega_{\rm c}^i K_{\rm nc}^i \right). \tag{6.7}$$

Here,  $C^{i}_{SC}$  is an effective near-field solubility parameter for radionuclide type *i*, accounting for the presence of sorbent colloids. Note that, as defined,  $C^{i}_{SC}$  accounts for the effect of organic complexants on radionuclide sorption to colloids but it does not account for the enhancement of radionuclide solubility due to organic complexation. The solubility enhancement factor,  $\xi^{i}$ , is applied to  $C^{i}_{SC}$  separately according to equation (6.6).

The possibility that the presence of organic complexants may stabilise and enhance the concentration of near-field colloids was recognised in the Nirex 97 assessment. This effect can be accounted for by increasing the colloid concentration used in the evaluation of the effective near-field parameters (equations (6.4) and (6.7)).

#### 6.2.3 Reference case scenario

The risk calculations undertaken to investigate the potential impact of colloids were based on two deterministic variants on the Reference Assessment Model in Nirex 97, which were designated R[G1] S3 B1 and R[G1] S1 B1 in the Nirex 97 notation. These variants differed in their treatment of organic complexants in the near-field as follows:

- Model S3, in which 100% degradation of the cellulose wastes (to yield organic complexants) was assumed to occur within a short timescale in the near-field, so that the impact of organics was maximised;
- Model S1, in which organic complexants were assumed to be consumed rapidly by microbial activity and, therefore, to have no impact on radionuclide transport in the near field.



Model S3 was deemed 'cautious' and Model S1 as more likely to underestimate their impact on dose. These variant models were used as the basis for the colloid variant (or alternative) calculations to investigate the influence that the presence of organic complexants in the near field may have on the impact of colloids. Although the impact of organic complexants was primarily on the source term in the assessment model, it was assumed that organic complexants would migrate into the far field before being diluted by mixing with the groundwater and consumed by microbial activity. Organic complexants advected from the near field could have a minor effect on the impact of far-field colloids [35].

The two colloid variant cases of the reference assessment models reported as part of Nirex 97, represented the then current best estimates for the behaviour of colloids in both the near and far-fields at Sellafield. In addition to these best estimate calculations, additional assessment calculations were performed to scope the effects of colloids on radiological risk in more detail. The effects of near-field colloid concentration, colloid exclusion and the effects of organic complexants in the repository were also investigated. Details of all these colloid variant cases are given in Reference [35].

#### 6.2.4 Data for the Treatment of near-field colloids

For the best estimate calculations, a population of  $10^{16}$  colloids m<sup>-3</sup> was assumed in the near field in the absence of organic complexants (S1) and colloid exclusion in the near field was assumed to be identical to that of anionic species. For the colloid case with organic complexants present in the near field (S3), a population of  $10^{18}$  colloids m<sup>-3</sup> was assumed, allowing for a 100-fold increase in the colloid population due to stabilisation by organic complexants. Sorption onto near-field colloids was assumed to be reversible and the near-field colloid sorption distribution coefficients were estimated by scaling from data for 50 percentile  $K_d$  values for freshly-cured NRVB. A scaling factor of 200 was used to account for the potentially greater available surface area of the colloids based on measured sorption data for uranium(VI) onto NRVB-derived colloids [27] compared to sorption onto intact NRVB [250].

#### 6.2.5 Treatment of ADZ colloids and near-field colloids in the far field

Following resaturation of the repository and leaching of the cementitious backfill, the rock adjacent to a repository will be contacted by alkaline groundwater. However, the effect of the alkaline groundwater on the surrounding rock in the alkaline disturbed zone (ADZ) was not treated in the Nirex 97 assessment as the nature, stability and mobility of colloids in the ADZ are uncertain. Therefore, near-field colloids in the ADZ were implicitly treated in the same way as far-field colloids. This included the assumption that far-field colloids are not stable or mobile in the near field. In addition, the assumption was made that the near-field colloids would dissolve or be destabilised on entering the far field (or ADZ) and release their radionuclide burden to the groundwater. This assumption was made because the equilibrium that may exist in the near field between colloid production and loss is lost once the near-field colloids are transported into the far field. Colloids in the near and far fields were therefore treated independently in the calculations.

#### 6.2.6 Best estimate calculations for the impact of colloids

Results of the deterministic risk calculations for the two reference models (with and without organic complexants present in the near field) are shown in Figure 6.2 and Figure 6.3 respectively. Each figure shows the total risk as a function of time for natural discharge to the Boreal Terrestrial biosphere model considered in Nirex 97 and the contributions from the most significant radionuclides. Note that the increasing uncertainties concerning the basis of calculations at times beyond  $10^4$  years imply that less confidence should be placed in the detailed quantitative results beyond this timeframe and so the figures are lightly shaded between  $10^4$  and  $10^6$  years and heavily shaded after  $10^6$  years.





Figure 6.2 Calculated risk and significant radionuclides contributing to risk for the Boreal Terrestrial Biosphere State for the deterministic variant of the Nirex 97 Reference Assessment Model R[G1] S3 B1, which includes organic complexants in the near field [35]



Figure 6.3 Calculated risk and significant radionuclides contributing to risk for the Boreal Terrestrial Biosphere State for the deterministic variant of the Nirex 97 Reference Assessment Model R[G1] S1 B1, with no organic complexants in the near field [35]

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Figure 6.4 Calculated risk and significant radionuclides contributing to risk for the Boreal Terrestrial Biosphere State for the colloid variant case N97 [S3] of the Nirex 97 Reference Assessment Model, which includes organic complexants in the near field [35]



Figure 6.5 Calculated risk and significant radionuclides contributing to risk for the Boreal Terrestrial Biosphere State for the colloid variant case N97 [S1] of the Nirex 97 Reference Assessment Model, without organic complexants in the near field [35]



Table 6.2Summary of peak risks and significant contributing radionuclides for the<br/>Boreal Terrestrial Biosphere State from deterministic variant calculations of<br/>the Reference Assessment Model in Nirex 97 with and without organic<br/>complexants present in the near field and with and without colloids<br/>(from [35])

Model	Peak Risks			Significant	
	0-10 <sup>4</sup> years	10 <sup>4</sup> -10 <sup>6</sup> years	10 <sup>6</sup> -10 <sup>8</sup> years	radionuciides	
R[G1] S3 B1 a	1.3 10 <sup>-14</sup> at 5 10 <sup>3</sup> years	7.2 10 <sup>-8</sup> at 4 10 <sup>4</sup> years	4.2 10 <sup>-8</sup> at 1.25 10 <sup>7</sup> years	<sup>10</sup> Be, <sup>36</sup> Cl, <sup>99</sup> Tc, <sup>129</sup> I, <sup>226</sup> Ra, <sup>230</sup> Th, <sup>232</sup> Th	
R[G1] S1 B1 b	1.3 10 <sup>-14</sup> at 5 10 <sup>3</sup> years	7.2 10 <sup>-8</sup> at 4 10 <sup>4</sup> years	2.1 10 <sup>-9</sup> at 3.2 10 <sup>7</sup> years	<sup>10</sup> Be, <sup>36</sup> Cl, <sup>99</sup> Tc, <sup>129</sup> I, <sup>226</sup> Ra, <sup>230</sup> Th	
N97 [S3] °	1.4 10 <sup>-14</sup> at 5 10 <sup>3</sup> years	7.2 10 <sup>-8</sup> at 4 10 <sup>4</sup> years	4.4 10 <sup>-8</sup> at 1.25 10 <sup>7</sup> years	<sup>10</sup> Be, <sup>36</sup> Cl, <sup>99</sup> Tc, <sup>129</sup> I, <sup>226</sup> Ra, <sup>230</sup> Th, <sup>232</sup> Th	
N97 [S1] d	1.3 10 <sup>-14</sup> at 5 10 <sup>3</sup> years	7.2 10 <sup>-8</sup> at 4 10 <sup>4</sup> years	6.3 10 <sup>-9</sup> at 2.5 10 <sup>7</sup> years	<sup>10</sup> Be, <sup>36</sup> Cl, <sup>99</sup> Tc, <sup>129</sup> I, <sup>226</sup> Ra, <sup>230</sup> Th	

Notes:

- a Deterministic variant of the Reference Assessment Model in Nirex 97. This includes organic complexants in the near field but colloids are omitted.
- b Deterministic variant of the Reference Assessment Model in Nirex 97 in which the impact of organic complexants in the near field and colloids are omitted.
- c Variant of case R[G1] S3 B1 (with organics) that includes the impact of colloids in both near and far fields.
- d Variant of case R[G1] S1 B1 (without organics) that includes the impact of colloids in both near and far fields.

Results for the two colloid variant cases, designated N97 [S3] (with organics and including the impact of colloids in both near and far fields) and N97 [S1] (without organics and including the impact of colloids in both near and far fields) were calculated. If colloids have an impact, it is expected to be on the transport of radionuclides with low solubilities in the near field and a strong tendency to sorb. Figure 6.4 shows the total risk versus time curve for the Boreal biosphere for the colloid variant case N97 [S3]. Compared to the case without colloids, Figure 6.2, colloids do not affect the peak risk arising from <sup>36</sup>Cl and <sup>129</sup>I after 40 thousand years because both may be considered non-sorbing. However, the risk arising from <sup>99</sup>Tc after ~10<sup>6</sup> years is increased by nearly one order of magnitude in each biosphere model in the presence of colloids and the risk arises slightly earlier. The peak risk arising from the <sup>238</sup>U decay chain daughters after long timescales is barely affected by the presence of colloids.

The peak risks calculated in each of the three timeframes  $(0-10^4 \text{ years}, 10^4-10^6 \text{ years} \text{ and } 10^6-10^8 \text{ years})$ , and the most significant radionuclides contributing to risk for the Boreal Terrestrial biosphere state for the four cases, are summarised in Table 6.2.



The results for the colloid case N97 [S1], with organics absent from the near field, are shown in Figure 6.5 and can be compared with the reference case R[G1] S1 B1 (Figure 6.3). For colloid case N97 [S1], the peak risk arising from  $^{99}$ Tc is increased slightly compared to the reference case. However, the increased risk for  $^{99}$ Tc is smaller than that calculated for case N97 [S3], where organics are included in the near field. This is due to the smaller concentration of near-field colloids ( $10^{16}$ m<sup>-3</sup>). In the absence of near-field organic complexants, the presence of colloids increases the peak risk arising from the  $^{238}$ U decay chain daughters at long times by only a factor of approximately three.

The risk calculations presented here show that, if a pessimistic view is taken concerning the extent of radionuclide complexation by organic degradation products in the near field, the likely impact of colloids present in the near and far fields at the Sellafield site, is negligible. However, should the situation arise that organic complexants are removed by significant microbial activity, colloids present in the near field could have an impact on the source term and increase risk arising from the <sup>238</sup>U daughters at long times. In addition, the possible significance of irreversible or time-dependent sorption processes to colloids was recognised as an uncertainty [35]. An additional uncertainty concerns the potential lifetime of colloids migrating from the near field into the geosphere and the assumption that near-field colloids will dissolve on migration into the ADZ.

#### 6.3 Wellenberg (Switzerland)

#### 6.3.1 Disposal concept and site

In common with Nirex, Nagra considered geological disposal for L/ILW, using a multi-barrier containment system [83]. Vaults would have been excavated at depth in a stable geological environment, but unlike in Nirex 97, access was planned to be horizontally to the 'in-mountain' repository in this Alpine area (Figure 6.6). The repository would have been constructed in the tectonically disturbed, fractured sediments of the Valenginian Marl (Palfris Formation, Figure 6.7). Wastes, packaged in steel drums then concrete containers, would be placed in the vaults, which would then be backfilled with a cement-based material (Figure 6.8).

Here, the discussion will focus on treatment of the potential impact of near-field colloids on radionuclide release via the groundwater pathway.

Nagra are no longer considering the Wellenberg site for a repository following an executive decision by the Swiss Federal Government (see [251] for a detailed discussion on the background to this decision).

#### 6.3.2 Near-field colloids

Arguably the most significant difference between the mathematical treatments of radionuclide migration in the Wellenberg and Nirex 97 assessments concerns the treatment of near-field transport. Whereas Nirex 97 modelled the near field as a homogeneous well-mixed system, the Nagra assessment included advection and dispersion of radionuclides with groundwater flow from the waste containers through the engineered barriers to the host rock. The potential impact of near-field colloids (generated from concrete, metal and waste components) on radionuclide release from the near field was considered as an "alternative modelling approach" from the reference case, which did not include colloids.

The model concept for radionuclide transport influenced by near-field colloids was kept as simple as possible. The aim was to describe, with cautious simplifications, the influence of near-field colloids on radionuclide release from the repository vaults. Consideration of certain processes which can have a positive impact on repository safety (e.g. colloid destabilisation and

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Figure 6.6 The Wellenberg site in central Switzerland, located south of Lake Luzern. viewed from the SSW, the mountainous terrain of the area is clearly shown; the repository would have been constructed under the mountain in the middle foreground (cf. Figure 6.7 and Figure 6.8); image courtesy of Nagra



Figure 6.7 Geological cross-section (approx. W-E) through the Wellenberg site, with the proposed repository area marked. Image courtesy of Nagra.







Figure 6.8 System of multiple safety barriers for the proposed Wellenberg L/ILW repository (top) and proposed repository 'in-mountain' layout with horizontal access (bottom, viewing from the SSE); images courtesy of Nagra

colloid filtration in the near field and in the far field) was dispensed with at the time because it was felt that relevant data were lacking (see Section 5.1.3 of [83]).

#### a) Simplified model concept

The model concept for colloidal-influenced radionuclide transport in the near field includes mobilisation of the radionuclides in the waste packages, transport of radionuclides through the repository EBS and release into the adjacent host rock. Transport of dissolved radionuclides and radionuclides sorbed on mobile colloids are described simultaneously.

The model concept is based on the following assumptions which were as similar as possible to the corresponding assumptions for the transport of dissolved radionuclides in the near field.

- On mobilisation, the radionuclides are distributed between the solid, the colloidal and the fluid phase. The distribution is assumed to be linear for all times and is quantified by element-specific distribution coefficients. In the model calculations, homogeneous distribution of the activity in the waste container interior is assumed at time t=0. Limitations of the radionuclide concentration in the fluid phase (solubility limitation) or on the colloidal phase (sorption capacity) were not considered; these were viewed as being cautious assumptions.
- The radionuclides are dissolved or sorbed onto mobile colloids and transported through the EBS. Two cases are distinguished:
  - Case 1: sorption of radionuclides on the colloids is reversible. The radionuclide distribution between the solid, colloidal and fluid phase is in equilibrium. The distribution is assumed to be linear and reversible and can be described using element-specific distribution coefficients. The distribution coefficients between the colloidal and liquid phases were estimated by applying a scaling factor ( $S_c$ ) to the distribution coefficient ( $K_{d,i}$ ) between the solid and liquid phases. Case 1 represents the 'base case' of the alternative modelling approach with consideration of near-field colloids.
  - Case 2: sorption on the colloids is irreversible, i.e. during transport there is no desorption of radionuclides from the colloidal phase.
- During their transport in the repository vaults, colloids are neither sorbed on the solid phase nor filtered in the pore spaces. This represents a cautious assumption.
- The colloid concentration in the repository vaults is assumed to be spatially and temporally constant, i.e. the colloids are newly formed to the same extent as they move from the repository vaults into the adjacent host rock.
- The advection rates of the colloids and the dissolved materials are assumed to be identical.

#### b) Consequences of near-field colloids for far-field transport

When investigating the consequences of near-field colloids for radionuclide transport in the far field, a distinction was clearly made in [83] between reversible and irreversible radionuclide sorption on near-field colloids as follows.

- If the radionuclide sorption on colloids is reversible, the radionuclide transport mechanisms in the far field remain unaffected, provided that the concentration of near-field colloids is sufficiently small.
- Under the assumption of irreversible radionuclide sorption on near-field colloids, three cases can be distinguished according to the stability of the near-field colloids in the far field.



- a) If the near-field colloids are dissolved on passing from the near field into the far field because of altered chemical conditions, the released radionuclides go into solution. In this case, the conceptual considerations relevant to far-field transport are identical to those for the reference case.
- b) If the radionuclides remain irreversibly fixed on the near-field colloids and the colloids are filtered out, a better barrier effect results than for the reference case. This possibility is not considered further.
- c) If the near-field colloids are also stable (and not filtered) in the far field, the irreversibly sorbed radionuclides are transported without retardation through the far field. This case is covered by the robust approach (see below).

#### 6.3.3 Results

#### a) Case 1 – reversible radionuclide sorption to colloids

In the case of reversible radionuclide sorption on colloids (Case 1), the influence of the near-field colloids in the entire repository can be described by an effective retention factor,  $R_{eff,i}$ , which depends on the material properties of the different hydraulic units of the near field. Details of the modelling approach and abbreviations are given in chapter 5 of [83] and, here, a few examples are provided:

- For cement mass,  $m_z = 1,350 \text{ kg m}^{-3}$ , porosity,  $\varepsilon = 0.25$  and for the scaling factors  $S_c = 100$  and 1,000, the dependence of the ratio  $R_{eff}$ ,  $i/R_i$  on the colloid concentration  $\chi$  and the  $K_{d,i}$  value, where  $R_i$  is the retention factor for radionuclide i unaffected by colloids. Here, the effective retention factor,  $R_{eff}$ , values for a colloid concentration of 1 ppm  $(10^{-3} \text{ kg m}^{-3})$  and  $S_c$  values of 100 and 1,000 are a maximum of 30 % and a factor of 6 respectively smaller than the retention factor unaffected by colloids,  $R_i$ . However, this maximum influence affects only the actinides from the waste group L/ILW-1 of [83], which are the only safety-relevant radionuclides with a  $K_d$  value of 5 m<sup>3</sup> kg<sup>-1</sup>.
- In all other cases (radionuclides with  $K_d$  value  $\leq 1 \text{ m}^3 \text{ kg}^{-1}$  waste groups L/ILW-1<sup>10</sup> to L/ILW-4 of [83]), the effective retention factor for a colloid concentration of 1 ppm and a scaling factor of 100 and 1,000 compared with the retention factor unaffected by colloids is a maximum of 10 % and a factor of 2 respectively smaller. The consequences for radionuclide release from the near field are also correspondingly small.
- In the case of reversible radionuclide sorption on colloids (Case 1), the release rate results indicate an approximate 10% higher release at slightly earlier times (for a hydraulic permeability of the host rock of 10<sup>-11</sup> m s<sup>-1</sup>, *K*<sub>d</sub> value of 1 m<sup>3</sup> kg<sup>-1</sup>, a scaling factor for the *K*<sub>d</sub> values of 100, a colloid concentration of 1 ppm and a cement mass m<sub>z</sub> dependent on the material properties of the hydraulic units).

#### b) Case 2 – irreversible radionuclide sorption to colloids

Model calculations of the influence of colloids on the fractional release rates were also performed for the case of irreversible radionuclide sorption on near-field colloids (case 2, above). For the container interior: a  $K_d$  of 1 m<sup>3</sup> kg<sup>-1</sup>, a colloid concentration of 1 ppm and a scaling factor of 100 were assumed. The hydraulic permeability of the host rock was assumed

<sup>&</sup>lt;sup>10</sup> According to [83], for long-term safety, maximum radionuclide retention in the near-field is desirable. This is achieved by emplacing separately wastes with components that may have an adverse effect on the immobilisation of radionuclides. The wastes assigned to the L/ILW repository in Switzerland were divided in four groups (L/ILW-1 to L/ILW-4), which will be emplaced in four separate areas in the repository. The division is based on how the chemical form of the waste might affect near-field radionuclide retardation.



to be  $10^{-11}$  m s<sup>-1</sup>. In all other hydraulic units of the near field, the retention factor was set as 1. Thus, once released from the containers, all of the radionuclides were assumed to be sorbed onto colloids and to migrate through the near field without retardation. In this case, the fractional release from the near field influenced by irreversible radionuclide sorption on colloids begins after about 10 years and reaches its maximum after 100 years. In contrast, colloidal-unaffected fractional release begins only after approximately 5000 years and reaches its maximum after more than  $10^5$  years. The maxima of both curves differ by around a factor of two.

It is notable here that the magnitude of the effect on fractional release rates appears to be comparable with that on peak risk found in Nirex 97 for the colloid case without near-field organics, which required no assumptions to be made concerning the reversibility of uptake to colloids.

#### c) Robust Case

With the aim of covering the uncertainties regarding the extent of sorption on the solid phase, additional model calculations (full assessment calculations) were performed in which sorption of radionuclides on the solid phase was omitted. This 'robust case' was based on an extremely cautious model assumption that all radionuclides in the near field are 'sorbed on colloids and are released without retardation'. Accordingly, this release curve lies around more than three orders of magnitude above the 'realistic curves for colloidal-influenced release'.

For this hypothetical assumption, dose rates were calculated for all radionuclides independent of their waste classification under the assumption of a host rock permeability of 10<sup>-11</sup> m s<sup>-1</sup> and a hypothetical direct radionuclide release into the biosphere model area of the Engelberg valley (far left of Figure 6.7). The maximum values are presented in Table 6.3, where, for comparison, the dose rates are listed for a near field with the reference dataset (without colloids) and a hypothetical direct release into the model area Engelberg valley. The dose rates for the model

# Table 6.3 Maximum summed doses for the waste groups L/ILW-1 to L/ILW-4: calculation with and without near-field sorption for a host rock permeability of 10<sup>-11</sup> m/s and a hypothetical direct release of radionuclides into the biosphere model area of the Engelberg valley (further explanations in text)

Waste group	Maximum summed	Dominant radionuclides <sup>3</sup>	
	Near field with sorption <sup>1</sup>	Near field without sorption <sup>2</sup>	
L/ILW-1	1.5 × 10 <sup>-₄</sup>	8.8 × 10 <sup>-2</sup>	<sup>63</sup> Ni, <sup>226</sup> Ra, <sup>210</sup> Pb
L/ILW-2	1.8 × 10 <sup>-3</sup>	8.1 × 10 <sup>-3</sup>	<sup>239</sup> Pu, <sup>241</sup> Am, <sup>14</sup> C
L/ILW-3	2.8 × 10 <sup>-4</sup>	1.3 × 10 <sup>-2</sup>	<sup>241</sup> Am, <sup>240</sup> Pu, <sup>239</sup> Pu, <sup>90</sup> Sr
L/ILW-4	-	5.9 × 10 <sup>-2</sup>	<sup>241</sup> Am, <sup>240</sup> Pu, <sup>239</sup> Pu, <sup>237</sup> Np

<sup>1</sup> Reference case near field (without colloids). <sup>2</sup>Covers the case where all radionuclides are sorbed irreversibly on [stable] colloids and these colloids have unrestricted mobility. <sup>3</sup> For the case of near field without sorption.



calculations without sorption in the near field lie, for all waste groups, below the Regulatory Protection Objective of 0.1 mSv year<sup>-1</sup> [252]. It was noted that: "*These extremely cautious model calculations cover the case of colloidal-influenced radionuclide release scenarios for the groundwater pathway, even if extreme colloid concentrations and sorption properties of the radionuclides on colloids are assumed.*"

Arguably, describing this extreme case as a 'colloid case' is something of a misnomer, as it is really concerned with the robustness of the safety case to the failure of engineered (backfill) and geological barriers to provide retardation due to sorption and is thus a bounding case for all processes that may be detrimental to radionuclide sorption. Such processes include complexation, mineralisation of solid surfaces, armouring of cracks and fracture surfaces with low porosity minerals, etc, as well as colloid transport. Therefore, it is important that this case is not over-interpreted in terms of the potential impact of irreversible sorption of radionuclides to near-field colloids.

#### 6.3.4 Conclusions

From the results of the model calculations for the alternative modelling approach with consideration of near-field colloids, it can be concluded for the case of reversible sorption on colloids (Case 1) that, for the assumed sorption properties and colloid concentrations, the colloids influence the near-field release only insignificantly. Also, for the subsequent far-field transport, the colloids are of secondary importance.

In the case of irreversible sorption on colloids (Case 2), for the cautious assumption of negligible colloid filtration, the following conclusions can be drawn.

In the case of irreversible sorption of radionuclides on near-field colloids, release of radionuclides from the repository vaults occurs earlier. If there is also significant sorption on the solid phase during radionuclide mobilisation in the container interior, colloidal-influenced [maximum] fractional release rates of the same order of magnitude as those in the reference case are expected. In an extreme case, where there is no sorption on the solid phase during mobilisation in the container interior - and therefore in all hydraulic units in the near field - additional model calculations were carried out that give higher fractional release rates. For these extremely cautious assumptions, where it is also assumed that the radionuclides are not retarded in the far field, the calculated dose rates lie close to of the Regulatory Protection Objective of 0.1 mSv year<sup>-1</sup>.

Thus the fractional release rates in the case of reversible sorption to colloids (Case 1) were not significantly higher than the fractional release rates of the reference case (without colloids) and it was always shown that, even with extremely cautious assumptions (no retardation due to sorption to immobile solids, and direct release to the biosphere), the dose rates are still of the same order as the Protection Objective. Consequently, no additional calculations were performed by Nagra at the time for the alternative modelling approach (taking into account near-field colloids) for the overall assessment of the proposed repository at the Wellenberg site.

#### 6.4 SAFIR 2 (Belgium)

The SAFIR 2 report [244] describes the progress made, between the publication of the original SAFIR report in 1989 and the end of 2000, in technical and scientific research related to the disposal of HLW/SF and long-lived ILW in horizontal galleries in a deep clay layer (the Boom Clay) in Belgium (Figure 6.9). In SAFIR 2, all the information and knowledge that has been collected is structured as it would be in a safety assessment, without it actually being a safety report. This is because it was not the aim of the report to make a license application, rather it was a state-of-the-art report along the lines of Japan's TRU-II report (see sub-section 6.5 for details).



Figure 6.9 Proposed layout of the repository for B (long-lived ILW) and C (heat-emitting HLW and SF) wastes in the Boom Clay of Belgium (from [254]).

In SAFIR 2, there is very little mention of colloids at all and absolutely none on near-field colloids, despite the fact that concrete is a significant part of the EBS (Figure 6.10). The assessment is very much focused on the properties of the host rock, because PA calculations for the normal evolution scenario (and for some altered scenarios) indicate that the key contribution to long-term safety is the performance of the Boom Clay [e.g. 253]. As noted in [254], "Boom Clay is by far the most dominant barrier, the near field playing a minor role...." and this is reflected throughout the report.

Although part of the waste stream is conditioned with bitumen, focus has been on organic complexants in the Boom Clay itself as it contains 1-3 wt% organic matter. Of this, little (around 0.05%) is assumed to be in solution and mobile. About half of this organic matter in solution, which consists of 70% humic acids and 30% fulvic acids and other small molecules, is characterised by a molecular weight of less than 1000.

Experimental data cited in [244] show that the presence of organic matter has no significant effect on far-field radionuclide migration because the mean pore diameter of the Boom Clay (5 nm) acts as an ultrafilter for the colloids and, in particular, for the organic colloids. This is significant as certain radionuclides (e.g. Eu, Am) are partially associated, thereby significantly limiting their mobility. Further, the organic matter sorbed on the surface of the clay minerals and retarded by the filtration in the clay has a high sorption capacity for the actinides. As this capacity seems to be highest for those fractions with the highest molecular weight, the sorption of those radionuclides on the immobile fraction should be significant.

Interestingly, an international review [255] of SAFIR 2 quoted directly from [244]: "An increase in temperature of the clay can also influence its mechanical properties (e.g. the degree of overconsolidation, rigidity, compression modulus) or can give rise to the formation of fractures and irreversible deformation." The review team noted that this area probably required further study but did not mention potential colloid-related release of radionuclides from the near field through the resulting fractures.

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### Figure 6.10 Cross section of part of the EBS in the proposed Boom Clay repository. Note the presence of significant quantities of cementitious buffer material (from [254]).

The potential effects of cementitious leachates from the EBS on the Boom Clay was scoped and, as in Project Opalinus Clay (see section 6.6), it was shown with a simple mass balance calculation (i.e. amount clay required to buffer the amount of cementitious material present) that no more than tens of centimetres of the host rock in the immediate vicinity of the C waste EBS should be disturbed. However, as the B waste stream galleries are back-filled with large amounts of hydraulic cement, the effect on the host rock and radionuclide migration [e.g. 10,256] is currently being studied further (although no specific mention was made of colloids).

#### 6.5 TRU-II (Japan)

The TRU-II report [17] is not dissimilar to SAFIR 2 in that it is not a detailed safety assessment, rather it should be seen as an update of a previous report [i.e. 257] which was part of an overall examination of radioactive waste disposal in Japan (Figure 6.11). The specific objectives of TRU-II can be summarised as follows.

- To build on the R&D of TRU-waste disposal using more realistic boundary conditions and up-to-date databases.
- To describe the progress on Japanese R&D related to TRU-waste disposal.
- To illustrate R&D priorities and focus, namely:
  - o bentonite-cement interaction models;

- methods to reduce the effects of waste nitrates, which are particularly voluminous in Japan;
- to introduce a newly developed top-down safety assessment approach (comprehensive sensitivity analysis); and
- to optimise approaches including co-location of TRU wastes with HLW (which is new in Japan) and alternative designs to immobilise and confine key radionuclides.
- To provide a technical basis in order to promote the establishment of a regulatory framework and an implementation body in Japan (at the time of writing the report, an organisation for implementing the geological disposal of TRU-waste had yet to be decided – NUMO was formally given responsibility by the Japanese government in April 2008).
- To highlight outstanding technical and managerial issues and to promote future domestic and international co-operation to help address and solve these issues.

#### 6.5.1 Disposal concept and site

Clearly, at this stage in a generic study, there is no specific site under consideration but design concepts have been developed and these have some defined boundary conditions. Based on a previous study [258], types of TRU waste may be disposed in one of four possible ways:

- near surface (typically several metres depth) disposal for TRU waste with the same alpha, beta and gamma activities as VLLW (from decommissioned reactors);
- shallow depth disposal (4–9 m) for TRU-waste with the same radionuclide content as LLW (from decommissioned reactors);



Figure 6.11 Timeline of R&D on radioactive waste disposal in Japan [from 17]

- intermediate-depth disposal (50-100 m) for TRU-waste with the same radionuclide content as relatively higher level LLW (from decommissioned reactors); or
- geological disposal (greater than 300 m) for TRU-waste with high (greater than all reactor wastes) alpha, beta and gamma activities.

With respect to host rock types, the range of generic hard (i.e. crystalline) and soft (i.e. sedimentary) rocks defined in the H12 study (see Figure 6.11 and [259]) were examined here, producing a range of potential EBS designs. Figure 6.12 shows a generic design for a geological cementitious TRU repository in Japan.

TRU wastes for geological disposal have been divided into four groups as follows:

- Group 1 spent iodine filters containing iodine-129, which would be immobilized by solidification in cement;
- Group 2 compacted hulls and endpieces, relatively high heat generating wastes that contain significant quantities of carbon-14;
- Group 3 bituminized or cemented concentrated process liquid waste with relatively large content of asphalt and sodium nitrate; and
- Group 4 all other wastes.

It is envisaged that each waste group would be disposed separately in a geological facility, as indicated in Figure 6.12. It will be noted that in the generic design, Group 1 and 2 waste vaults would be surrounded by a bentonite buffer but Group 3 and 4 vaults would not.



Figure 6.12 Example generic design for a cementitious TRU repository in Japan [from 17]



#### 6.5.2 Base Scenarios

Scenarios related to the safety assessment were constructed from FEPs that were not excluded by screening. The relationship between the scenarios considered is illustrated in Figure 6.13. The scenarios of principal interest here are the groundwater scenarios, which were divided into a Base Scenario, where it is assumed that the present geological and geomorphological conditions remain unchanged and a perturbation scenario where future changes are assumed. The Base Scenario was divided further into a Reference Scenario and an Alternative Scenario.

The Reference scenario is based on FEPs connected with the initial conditions of the disposal system (e.g. groundwater chemistry) and those FEPs that are assumed to arise or operate in specifying the safety performance of the facility (e.g. leaching of radioelements from waste packages). The Alternative Scenario includes FEPs that may have an influence over the safety performance of the disposal system but where their influence is more uncertain. The relationship between the scenarios and their related FEPS is summarized in Table 6.4.

The effects of near-field colloids are explicitly included in the FEP list, covering the waste, cementitious backfill, vault structural components, the bentonite buffer and in plugs and grouts. However, in the Reference Scenario, using the FEP screening methodology of H12 [259], where the FEPs were so screened (see also Table 6.5):

- "it is judged [assessed] that the effects [of colloids] can be avoided by site selection;
- *it is judged that the influence* [of near-field colloids] *can be avoided by engineering measures;*
- *it is judged that there is an extremely low probability of occurrence* [of near-field colloids]; *and*
- *it is judged that there is only a small influence* [of near-field colloids] *on the disposal system.*"

Thus, the influence of colloids was screened out of the Reference Scenario, based on "....the result of a standardised, rational judgement." [17] and "The treatment of these FEPs is not discussed here (further)."

In the Alternative Scenario, however, colloid-facilitated transport is explicitly considered viz: *"Radionuclide migration is influenced by colloids, organic matter (natural) and microbes"*.

The Perturbation Scenario focuses on natural and anthropogenic perturbations such as uplift and erosion, climate change, drilling of water wells that short circuit migration pathways, etc; near-field colloids are not explicitly considered.

The Isolation Failure Scenario effectively looks at more extreme versions of the Perturbation Scenario with, for example, erosion causing the repository to be exposed at the surface or drilling directly into the repository.

#### 6.5.3 Modelling approach

#### a) Base Case Reference Scenario

Radionuclide transport analyses and dose assessments were performed using an existing deterministic approach [260] and a newly developed, top-down, assessment approach [261], to assess uncertainty better.

In the EBS, waste packages are present, but no retardation effect of the package is taken into account. Hence, radionuclides are assumed to dissolve rapidly (with the exception of activation products in stainless steel and ends such as zircaloy) and migrate into the cementitious backfill.



### Figure 6.13 Scenarios for radionuclide release to the human environment evaluated in TRU(II)

For the near-field source term, solubility control is assumed for the Group 1 and 2 wastes (cf. Figure 6.12), but not for Groups 3 and 4 "....and the effects of colloid formation are considered from a cautious point of view." [17], although it is not clearly stated what this implies. On transport out of the cementitious backfill, near-field colloids are presumed filtered by the bentonite buffer – but note that Group 3 and 4 wastes vaults have no bentonite buffer and here the potential effects of colloids are covered by the cautious assumption that there is no precipitation of radionuclides in the EBS.

#### b) Base Case Alternative Scenario

As noted above, colloids are explicitly included in this scenario, but not near-field colloids *per se*. First, although alteration of the buffer is included, this is focused on changes to the sorption capacity of the material and does not include changes to the colloid filtration ability (i.e. there is an implicit assumption that colloids are filtered out, although this is not clearly stated). Second, the colloids which are addressed are far-field colloids, where the H12 assumptions are used to assess colloid-induced radionuclide migration in the fractured host rock. Interestingly, gas expulsion of radionuclides in near-field leachates is assessed and, although it is noted that gas could induce new flowpaths through the bentonite buffer, this does not appear to be directly addressed (i.e. once again, implicit filtration of near-field colloids).

#### c) Perturbation Scenario

Although initial defects in the EBS are considered, near-field colloids are not explicitly included in the analysis.



#### Table 6.4 Summary of scenarios and FEPs assessed in the TRU-II safety calculations (Table 4.3.6-1 of [17])

FEP Type	Summary FEPs	Scenario Type	Scenario sub-type	Scenario sub-sub-type	Important environmental conditions etc for safety assessment	Corresponding report section	
FEPs concerned with the preconditions of the disposal system	Thermal environment		water Scenario	Reference Scenario (Representative Scenario)	Temperature influence	3. 2. 3. 3	
	Hydrogeology				Hydraulic field (re-flooding)	4.4.4	
	Mechanical stability of the host rock Mechanical stability of plugs etc Mechanical stability of engineered barrier materials Swelling of the buffer Decrease in density of the buffer Corrosion expansion of engineered harrier materials Waste packages/structural members movement and settling	-			Mechanical conditions	3. 3. 2	
	chemistry				Groundwater chemistry	4.4.1	
	Radiological analysis/radiation damage				Radiological effects	4.4.8	
	Organic matter (included in the waste)				Effects of organic matter (Contained in waste)	4.4.6	
	Nitrate				Effects of nitrate	4.4.9	
FEPs connected with the assumed/specified safety function of the disposal system	Release of nuclides from the waste Precipitation and dissolution Sorption Diffusion and dispersive advection Nuclide migration in the EBS Nuclide migration in the host rock	Groundwater Scenario			Nuclide migration	4. 5. 2	
FEPs that influence the safety fuinction of the supposed/ specified disposal system	Alteration of buffer material Alteration and fracturing of			Alternative scenario	Effects of altertation of engineered barrier materials	4.4.2	
	Allesing alteration of the best work				Alkaline alteration of surrounding host rock	4.4.3	
	Hydrogeology of the engineered barrier				Hydrogeological conditions of the near field (influence of geochemical alteration)	4. 4. 4	
	Production and migration of colloids				Effects of colloids	4.4.5	
	Organic matter (Natural)				Effects of organic matter (natural)	4.4.6	
	Microbes				Effects of microbes	4.4.7	
	Unradioactive gas/radioactive gas				Effects of gas and nuclides in gaseous form	4.4.10	
FFPs that harm the safety	Natural phenomena		Perturbation Scenario	Scenario concerned	Uplift and erosion		
function in the supposed/specified disposal system				with natural phenomena	Climate change, Sea level change		
	with engineered components			Scenario concerned with initial defects	Seal failure	4. 5. 5	
	Future human activity			Scenario concerned with future	Well drilling and water extraction		
	r uture multian activity			human activities	Formation of new migration paths by boring		
FEPs that possibly	Natural phenomena			Natural phenomena scenario	Uplift and erosion	4.5.6	
function of the supposed/		Isolation Failure Scenario		Hypothetical scenario	Volcanoes, Magmatism (Magma intrusion)		
specified disposal system	Future human activity			Future human activity scenario	Future accidental human intrusion	4, 5, 6	

Table 4.3.6-1 Types of FEPs, summary FEPs, scenarios and repository conditions that are important for safety assessment

### Table 6.5 Extract from Table 4.3.3-2 of [17] which explains the screening of the near-field colloid FEPs

FEPs for which judgment	Grounds for reservation	
Influence of colloids in the disposal facility WC-08/MC-07/	[Explanation of exclusion] From experiments, it has been confirmed that compacted bentonite can filter metal colloids ( $\phi$ 15 nm) (Kureanus et al. 1997). In the case where a layer of bentonite is included in the dimensionement it is	
SC-07/BC-07/XC-07 WN-07/MN-06/ SN-06/BN-06/XN-06	considered that colloids produced in the engineered barrier system will be filtered by the bentonite. In cases where there is no layer of bentonite, and cementitious materials are used as a filling and in structural components, general colloids will be unstable under the pore water conditions. It is suggested that the concentration of these colloids will be low and their influence on nuclide sorption will be small.	
	[Explanation for selection]	
	In the case where a layer of bentonite exists	
	(Dependent on the influence of variations in alkali conditions) in the case where smectite dissolution and decrease in abundance is assumed, the expected filtration by the layer of bentonite may be compromised. There is then a possibility that colloids produced in the engineered barriers will penetrate.	
	In the case where a layer of bentonite does not exist	
	There is a significant quantity of colloids in the cement pore water. Furthermore, because colloids are produced by disturbances to the groundwater, in this situation (for example, influences of excavation, etc.), the production of colloids caused by repository construction cannot be ruled out.	

#### Table 4.3.3-2 Two arguments concerned with FEPs for which judgment is reserved

#### 6.5.4 Co-location of cementitious wastes with HLW

Here, a reasonably detailed analysis of the potential impacts of a cementitious TRU repository on a co-located HLW repository has been carried out. For cementitious near-field colloids, it is noted that "The effect on an HLW disposal facility of mass transfer by cement colloids originating in the TRU waste disposal facility is also small. If the analysis of the high-pH plume ensures a sufficient isolation distance, the effect of cement is sufficiently covered."

For organic materials (although it is considered that these are in solution, rather than in colloidal form), an appropriate respect distance between the two repository types should also ensure little or no impact.

#### 6.5.5 Conclusions

It was noted in the report that the colloid model utilised assumes linear instantaneous sorption of radionuclides by colloids, but goes on to state that "....*at present there is no reliable model for the effect of colloids.*" However, here the authors are really discussing far-field colloids and only (implicitly) turn to near-field colloids when commenting "*In addition, the chemical forms of radionuclides that migrate from the waste are not uniform. Hence, for assessing the effects of colloids, data for each radionuclide needs to be accumulated and reflected in the radionuclide transport analysis."* 

Interestingly, when carrying out a 'comprehensive sensitivity analysis' of those parameters which are assumed to have a significant impact on dose, it was noted that "....safety is not compromised by the effects of engineered barrier degradation, colloids, gases and initial oxidizing conditions.", although it should be noted that this analysis considers both near- and far-field colloids together. Where organic material is considered, it is generally focused on the impact of natural organics in the far field.

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#### 6.6 **Project Opalinus Clay (Switzerland)**

#### 6.6.1 Introduction

The Project Opalinus Clay (POC) safety assessment [79] contains relatively little discussion of colloid-facilitated transport of radionuclides and, from the viewpoint of near-field colloids, is similar to SAFIR 2 (sub-section 6.4). The stated aims of POC were to:

- determine the suitability of the Opalinus Clay of the Zürcher Weinland in northern Switzerland as a host rock for the repository from the point of view of long-term safety;
- enhance the understanding of the multiple safety functions that the proposed disposal system provides;
- assess the robustness of the disposal system with respect to remaining uncertainties and the effects of phenomena that may adversely affect the safety functions; and
- provide a platform for the discussion of a broad range of topics related to repository development. More specifically, the findings from the safety assessment, together with those from the regulatory authorities' review thereof, will provide guidance for future stages of repository planning and development.



Figure 6.14 Layout of the proposed SF/HLW/ILW repository in the Opalinus Clay of northern Switzerland [from 79]. Note the physical separation of the SF/HLW and the cementitious long-lived ILW (planned to be several hundred metres). For scale, the ILW vault (inset, right) is 8.5 m in diameter POC investigated building a repository for the co-location of SF (including MOX), HLW and long-lived ILW (cf. section 6.2.6) in the Opalinus Clay Formation. This host rock was chosen because:

- it has such a low hydraulic conductivity that solute movement through the formation is predominantly by diffusion rather than advection
- the geochemical conditions in the host rock are reducing, slightly alkaline and moderately saline and favour the preservation of the EBS and significant radionuclide retention
- the geochemical environment in the host rock and surrounding formations is expected to remain effectively stable for several million years
- only a minor salinity decrease is expected to occur over this timescale
- the Opalinus Clay is an indurated claystone (clay shale) with reasonable engineering properties, allowing small, unlined tunnels and larger, lined tunnels to be constructed at depths of several hundred metres (Figure 6.14)
- the properties of the Opalinus Clay ensure that repository-induced and natural fractures will be of very low hydraulic conductivity due to the self sealing capacity of the clay

Colloids do not feature greatly in POC for similar reasons to those given in SAFIR 2, namely the excellent isolation qualities of the host rock. As noted in [80], colloids exist in Opalinus Clay porewater but are expected to be virtually immobile, due to:

- the small pore size (mainly in the 1-25 nm range, but up to 100 nm [262]);
- poor pore interconnectivity;
- the low water content in the pores;
- charge exclusion owing to electrostatic repulsion between charged surfaces of the clay platelets and colloids effectively filtering out colloids (cf. section 6.4);
- moderate ionic strength of the porewater inducing colloid instability;
- a lack of high permeability fractures in the Opalinus Clay.

This is also thought likely to limit microbial activity too [263], so minimising the production (in the far field, at least) of biocolloids.

#### 6.6.2 Colloids in the cementitious near field

The FEP list for the cementitious near field is set out in [264] and the essential approach was not to assess processes in isolation, rather detailed FEPs were grouped into Super-FEPs with a Reference Realisation and Alternative Realisations (to reflect uncertainties, as seen in the approaches discussed above). It is noticeable that, as with SAFIR 2, many near-field FEPs are discarded based solely on the assumed performance of the far field. With respect to near-field colloids, the NEA International Review Team found this approach reasonable as they noted [265] ".....colloids are assumed to be immobile in the bentonite and the Opalinus Clay and do not contribute to enhanced transport. This assumption is supported by a technical report [80] and is reasonable given the filtration properties of clays."

Of additional interest is that the effects of the so-called 'alkaline plume' (Figure 5.1) have been addressed [266] in a more rigorous manner than has hitherto been the case. Here, the treatment concluded that the possibility of a sharp gradient in pH at the plume leading edge suggests that oversaturation or even supersaturation with respect to secondary minerals such as CSH, CASH or zeolites will occur (at least locally).


## Table 6.6 Cautious estimate of the extent of host rock (OPA) alteration around a cementitious ILW vault [from 266]

Buffering capacity	Ratio ILW/OPA	Affected volume of OPA	Thickness of hol- low cylinder around ILW
100 %	4:1	14.2 m <sup>3</sup>	0.5 m
10 %	4:10	142 m <sup>3</sup>	3.7 m
1 %	4:100	1420 m <sup>3</sup>	17 m



## Figure 6.15 Schematic representation of alteration of the Opalinus Clay host rock by diffusive transport of alkaline leachates from the cementitious ILW [from 266]

Colloid formation is favoured at such zones of supersaturation, especially where low temperatures kinetically hinder precipitation (see also Section 1). As laboratory experiments and natural analogue data indicate that these colloids will be of a similar composition to the secondary phases which will precipitate in the alkaline plume, they could potentially mobilise a significant radionuclide load. However, such are the properties of the Opalinus Clay host rock that transport of any such colloids beyond the ADZ is deemed highly unlikely in the assessment.

More generally, the FEPs associated with the alkaline plume have been treated in a manner similar to the SuperFEPs, with the far field performance having the greatest weight. This was supported by scoping calculations [266] of the buffer capacity of the host rock in the vicinity of



the cementitious ILW (cf. sub-section 6.4). Based on laboratory experiments on the host rock (e.g. [95] and Figure 6.15), it was possible to calculate the thickness of Opalinus Clay liable to be altered by the cementitious leachates from the 8.5 m diameter ILW vault (tunnel volume of  $57 \text{ m}^3 \text{m}^{-1}$ ). As can be seen in Table 6.6, the total volume is likely to be no more than a minor portion of the 150 m thick host rock (cf. Figure 6.15).

#### 6.6.3 Colloids in the near field of the SF/HLW repository

After saturation of the bentonite by groundwater following repository closure, the hydraulic conductivity was assumed to be  $< 10^{-12}$  m s<sup>-1</sup>, inferring that any radionuclide transport will be predominantly by diffusion through pores in the bentonite [79]. Colloid-associated radionuclides may be formed during SF/HLW dissolution, by precipitation of insoluble radionuclides or by coprecipitation and sorption processes. Here, as in the Opalinus Clay itself, the small pore size of saturated, compacted bentonite is assumed to prevent colloid (and high molecular weight species) transport [267]. In the cases that the bentonite buffer's performance is compromised (e.g. by gas transport through the bentonite), it is assumed that the host rock will effectively prevent any further colloid transport.

#### 6.6.4 Co-location of cementitious ILW with SF/HLW

As with TRU-II (see sub-section 6.5.4), ensuring an appropriately large respect distance between the two waste types provides sufficient protection for the SF/HLW repository from any near-field leachates and associated colloids. Interestingly, although gas-induced (or associated) release of dissolved and volatile radionuclides was directly assessed [268] and noted as being 'negligible', gas-induced colloid transport was not examined.

#### 6.6.5 Conclusions from POC

Although the question of near-field colloids has been investigated in POC in greater depth than in SAFIR 2, the conclusions reached in the assessment are not dissimilar, namely that the high isolation capacity of the far field means that most near-field colloid FEPs can be screened out at an early stage of the process.

#### 6.7 Conclusions

From the discussion above it will be clear that in those assessments where dose calculations were undertaken, highly cautious assumptions regarding the near-field colloids produce little increased dose, usually less than an order of magnitude greater than the Reference Scenario calculations. The only case of real significance is that of the Wellenberg Robust Case calculation which showed doses approaching the Regulatory Protection Objective of 0.1 mSv year<sup>-1</sup>. However, this was for an extreme, bounding case for geosphere transport, assuming as it did that there was absolutely no retardation of radionuclides in the far field. It is potentially misleading that the underlying process invoked was that all radionuclides were sorbed irreversibly to unretarded colloids, it could equally be described as unretarded solute transport. Given the extreme scenario, the results should not be overinterpreted in terms of the potential effects of colloids.

It was noted in Section 2 that intercomparison of data on near-field colloid populations is difficult owing to the variety of laboratory methods employed and this is very much the case here too. The assessments reviewed range from cases where near-field colloids have been examined in great depth, including providing radionuclide distribution coefficients (e.g. Nirex 97), through those where the source-term is slightly less well defined, but a detailed assessment was nevertheless carried out (e.g. Wellenberg) to those where near-field colloid FEPs were screened out at a very early stage (e.g. SAFIR 2, TRU-II). Where near-field colloids are rapidly screened out, the reasons are effectively the same: either the buffer (bentonite) or the host rock (plastic or indurated clay) can reasonably be assumed to filter most colloids from solution.



Where the host rock is a clay of some form, scoping calculations indicate that repository alkaline leachates will not induce significant damage to the host rock and so the filtration role will be maintained. There is less certainty for the case of the bentonite buffer or backfill in a cementitious repository, but this is being addressed by ongoing work in several programmes internationally (e.g. the Long-term Cement Studies experiment in the Grimsel URL [269]). However, the aim is to define minimum thicknesses of bentonite required rather than to focus on processes such as near-field colloid migration through a corrupted barrier.

It is noted that although transport of radionuclides in gaseous form via a gas pathway has been examined in several assessments (e.g. Nirex 97 [36]), gas transport of colloids has not been assessed. This is not to say that the process is being ignored, rather it is simpler to assess if gas transport *per se* could be of concern first before looking at gas-related colloid transport.

Finally, it is noted that, in the two cases where an NEA-constituted International Review Board examined an assessment, there was little or no discussion of colloids in either the near or far fields. In the case of the SAFIR 2 assessment, the Review Board noted that potential (heat-induced) fracturing of the clay should be further studied. However, the possibility that this could provide a means for colloids to 'short-circuit' the clay's colloid-filtering ability by this route was not discussed. Should heat-induced fracturing of clay prove to be an issue for these repository concepts, and the issue could not be readily mitigated by changing the facility design, then the arguments for omitting near-field colloids from the assessments of these concepts would need to be reviewed.

## 7 State of the Science

# 7.1 Current understanding of key questions concerning colloids in the near field

It has been more than a decade since the Nirex 97 PA, so it is appropriate to ask what progress has been made in understanding the key questions regarding near-field colloids in that time? There has been clear progress in many areas and, even in those where little material progress has been made, there has generally been identification of the key aspects which require further investigation.

Current understanding in each of the main areas covered in Sections 2, 3, 4 and 5 can be summarised as follows.

#### **Colloid Presence**

- Laboratory studies of near-field colloids to date have focused on colloid generation from cementitious backfill materials (NRVB, M1, HFSC) because these materials will dominate the mass and volume of components in a cementitious ILW/LLW repository.
- Concentrations generated from degradation of fresh cement materials are low with highest measured values of about 10<sup>12</sup> particles dm<sup>-3</sup> (in the size range 10 - 1000 nm for HFSC-derived colloids at low solid to liquid ratio). For NRVB, colloid populations released from monoliths over timescales of up to 31 months were in the range 10<sup>10</sup> to 10<sup>11</sup> particles dm<sup>-3</sup> for the greater than 50 nm size fraction.
- However, owing to limitations of the conventional colloid characterisation techniques that have been used to date for quantifying the smallest size fraction of the colloid populations, there is uncertainty concerning the potential contribution of the smaller particle size fraction. This may be important as the smallest particles are likely to have the largest surface area to mass ratio and may be significant with regard to available surface sites for radionuclide sorption. However, the use of 30,000 NMWCO filters to define the solution phase in radioelement solubility experiments will mean that, by definition, the effects of the smallest- sized colloids (1-3 nm) are accounted for in near-field solubilities. The potential significance of remaining size gap could be scoped by a systematic filtration study of radionuclide distribution between colloidasize fractions in cementitious leachates.
- 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 leaching experiments.
- In general, colloid concentrations measured for a given size range are considered to be cautious compared to cement porewaters in a repository due to aspects of the experimental methods employed. In particular, the lower solid to liquid ratios used in experiments compared to a repository, the effects of agitation and crushing or cutting applied to solid materials used in leaching experiments, flow rates used in column experiments, and the formation of artefacts during specimen preparation for colloid analysis will all tend to enhance colloid populations in (or measured in) experiments.
- Two combined waste equilibrium leach tests (ELTs) have shown that a range of colloid types may arise from interactions of cement materials with waste components; however, measured leachate colloid concentrations in supernatant leachates were also low, about 10<sup>10</sup> particles dm<sup>-3</sup>, (100 - 5000 nm size fraction) for supernatant leachates

and less than 10<sup>11</sup> particles dm<sup>-3</sup>, (100 - 5000 nm size) for drained leachates, in common with batch leaching experiments on cured NRVB.

- Brucite (magnesium hydroxide) colloids, arising from the degradation of waste Magnox components, which were present in ELT2 in the absence of significant quantities of NRVB were not found in ELT1 which contained NRVB in representative proportion to waste components. The stability behaviour of brucite colloids has yet to be sufficiently understood.
- In general, there is limited understanding of the potential for and extent of colloid generation from the interactions of waste components with cement porewaters, from cementitious grouts or from aged cements.
- Nevertheless, the colloid concentrations measured in short-term, small-scale laboratory examples are supported by low colloid concentrations (1-5 10<sup>10</sup> particles dm<sup>-3</sup>) 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, aged cement system. The findings add weight to the contention that the laboratory data are cautious.
- Typical groundwater colloids, such as aluminosilicates, iron oxides and humic acids are not expected to enter the near field in significant concentrations due to the gradients in calcium concentration experienced at the geosphere/near-field interface<sup>11</sup>. However, the specific nature of the colloid populations in the groundwater that may potentially enter a repository is a site-specific issue and should be addressed in future site characterisation programmes.
- At present there is limited understanding of the potential for colloid formation in the ADZ of the host rock surrounding the repository. 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. 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.

#### **Colloid Stability and Mobility**

- Owing to the low colloid concentrations measured in batch leaching studies, little direct work on the stability and mobility of cementitious near-field colloids has been possible. The majority of work has been undertaken on simulant model colloid systems or on crushed cement materials.
- Measured zeta potentials for a range of cement minerals and for simulant near-field colloids in the presence of cement-equilibrated waters are typically below about ±50 mV and usually less than ±25 mV. These values are considered to be too low to stabilise colloids in the long term at expected near-field calcium concentrations (typically above 10<sup>-3</sup> mol dm<sup>-3</sup>). Therefore, most of the colloid types that may form in the repository near field as a result of erosion, spallation or re-precipitation processes are expected to be destabilised under near-field conditions. Destabilisation will lead to aggregation and sedimentation of colloids and/or a tendency for colloids to attach to solid surfaces.
- 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. Thus the colloid populations in deep groundwaters are controlled by the

<sup>&</sup>lt;sup>11</sup> As noted elsewhere, the lower molecular weight fulvic acid fraction may potentially be mobile in the near field of a cementitious GDF, however, such species are not colloidal.



water composition which controls the rates of particle aggregation. Measured populations are considered to represent an equilibrium between colloid generation and loss (due to aggregation and sedimentation). The above relationship appears to hold also for high pH near-field conditions and provides an explanation for the low colloid number concentrations measured in experiments.

- The effect of calcium concentration controlling near-field colloid populations is expected to be general and to operate for the majority of inorganic colloid types that may arise under near-field conditions.
- 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. In the case of a cementitious repository, natural humates present in groundwater are not expected to be present at significant concentrations due to their insolubility at high pH and calcium concentrations typical of the near field, although lower molecular weight fulvates may be present. 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 to stabilise colloids under near-field conditions. Leaching of the M1 backfill in the presence of ISA, the major degradation product of cellulose under alkaline, anaerobic conditions, indicates that sorption of ISA onto the backfill does have an effect in stabilising colloid population and reducing the rate of colloid aggregation. However, the effect is too small to have a significant effect on colloid populations in the long-term. This finding is supported by the low colloid populations measured in equilibrium leach tests that included both cementitious materials and real or simulated wastes. There is no indication for enhanced colloid populations over the timescales (2-6 years) for the waste inventory and conditions in these tests as a result of colloid-organic compound interactions. Further work on the potential impact of organic degradation products on near-field colloid populations would build confidence in the understanding of this issue. It should be noted, however, that stabilisation of colloids by organic wasteform-derived components is considered to be of secondary importance compared to the impact of organic complexants on radionuclide solubility and sorption behaviour in the near field.

#### Radionuclide uptake

- Owing to the low colloid concentrations measured in batch leaching studies, there has been little direct work on sorption to near-field colloids, with only one published data point to date. Some information comes from studies using corrosion product stimulant colloids under near-field conditions and from two combined waste ELTs.
- One data set for U(VI) sorption onto NRVB-derived colloids suggests significantly stronger sorption to cement colloids than to intact cements. This finding is consistent with results for geosphere colloids compared to crushed rock, which reflects the higher surface area expected to be available for sorption onto colloid surfaces compared to bulk solids. However, further comparative data for radioelement sorption onto cementderived colloids and bulk cements would be necessary to build confidence in this finding should treatment of near-field colloids be required in future performance assessments.
- The results of two ELTs have shown clear association of alpha-activity with particles and solid surfaces. However, the amount of alpha-active radioelements (principally <sup>241</sup>Am and <sup>239/240</sup>Pu) associated with dispersed colloidal particles in leachates was very small compared to that present in solid phases. Colloid-associated beta activity (principally <sup>90</sup>Sr) was negligible compared to dissolved activities. There was little indication for significant radionuclide association with the smallest particle-size fraction (<0.45 μm) in the tests.</li>



- The relationship between the available surface area (i.e. available concentration of sorption sites per unit mass) to particle size for near-field colloids has yet to be clearly established. A cautious assumption is often made that particles can be approximated as hard spheres and that the surface area scales as the square of particle radius. In practice, however, near-field colloidal particles have been observed in a variety of shapes (spheroids, rods, flakes), may be composed of aggregates and larger particles may possess intergranular porosity. Thus the hard-sphere model may be an over-simplification.
- The reversibility of sorption of radioelements to colloidal particles and to solid phase surfaces is an area of ongoing research on the NDA RWMD programme and internationally. Some of the processes by which radioelements may be incorporated (i.e. removed from sorption equilibrium with the solution phase) into colloidal particles have been described conceptually. However, there remains limited understanding of the operation of such processes in practice. In particular, for strongly sorbing and weakly soluble elements such as thorium and plutonium, which are of most interest in the context of colloid facilitated transport, sorption reversibility is difficult to study experimentally. No work has been undertaken on near-field colloids directly although work on the reversibility of sorption to cements has been undertaken recently in Switzerland. Evidence for the incorporation (irreversible sorption) of radioelements into natural colloids has come from uranium series isotope distribution studies applied to colloid populations in groundwaters at natural analogue sites such as the Cigar Lake uranium ore body in Canada. 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.
- Irreversible sorption or incorporation of radionuclides into near-field colloids would not
  occur in isolation however. It is expected that similar processes would arise to
  incorporate radioelements into bulk cement phases. Given that spallation of mineral
  grains from cement surfaces appears to be a significant mechanism for colloid
  generation from cements, incorporation of radioelements into bulk cement phases may
  lead to the generation of colloid populations that contain embedded radionuclides.
- Although uranium particles were found in fast settling fines recovered from the two combined waste ELTs, no uranium- or plutonium-rich particles could be identified in leachate colloid populations. The uranium particles observed in the fines were too large and dense to form stable colloidal dispersions. There was no evidence for the generation of significant numbers of stable intrinsic radioelement colloids over the seven-year timescale of the tests.

#### Migration into the far field

- Due to the limited stability of colloids in the 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.
- Colloidal particles are thermodynamically metastable with respect to bulk solid phases owing to their higher surface free energy, which increases with decreasing particle size. As a result, smaller particles will tend to dissolve while larger particles or solid phases will grow preferentially. Therefore, it is expected that near-field cementitious colloids would dissolve on migration from a high pH near field to the low pH of the geosphere. However, this process has yet to be demonstrated experimentally for cementitious colloids. The persistence of colloids that migrate through a change of chemical conditions will depend on their solubility in the solution in which they are suspended, their size and rate of dissolution.
- Attachment of particles to the surfaces of gas bubbles (flotation) or the entrainment of colloids with a separate LNAPLs phase which may then migrate out of a repository by buoyancy-driven flow, provide potential mechanisms by which colloidal particles could



migrate out of the near field. These mechanisms will only be significant for colloidal particles that are hydrophobic in surface character and preferentially wetted by oil (or air) rather than water. Some common minerals have natural hydrophobic (non-ionic) surface character including graphite, sulphur, talc, pyrophyllite and other clay minerals with limited substitution of silicon atoms by aluminium in silicate layers (this excludes montmorillonite), and could potentially be floated or entrained in LNAPLs naturally. Hydrophilic minerals, such as metal oxides and CSH gels, however, would require stabilization with surfactants that change the wetting characteristics of their surfaces to enable dispersion in LNAPLs or flotation with gas bubbles. Gas will be generated in a repository as a result of corrosion of metals and the microbial degradation of organic materials; whether or not separate LNAPLs phases will form as a result of the release of as-disposed NAPLs or organic degradation is a current uncertainty and the subject of ongoing research on the NDA RWMD programme. Currently, there is little information available concerning the likely presence and formation of potential surfactants within a UK ILW repository. Given the uncertainties surrounding these processes, an assessment of whether or not they may be significant is not yet appropriate. In reality, colloid transport by flotation will be of secondary importance to repository safety compared to gas migration.

 At present there is limited understanding of the potential for colloid stability and mobility in the ADZ of the host rock surrounding the repository. 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 through the ADZ.

#### 7.2 Current understanding of potential impact of colloids in the near field

Current understanding of the potential impact of near-field colloids of the performance of a deep cementitious repository in the UK is based on the colloid variant case calculations undertaken as part of the Nirex 97 assessment. Owing to the treatment of the near field as a homogeneous, well-mixed system and the associated assumptions of colloid stability and mobility within the near field, these variant case calculations provide a cautious assessment of the potential impact of near-field colloids regardless of the reversibility of radionuclide sorption to colloids. These calculations found that the presence of near-field colloids could potentially increase the calculated radiological risk at very long times arising from the <sup>238</sup>U daughters. In addition it was recognised [35] that near-field colloids may potentially increase the source term of other radionuclides in addition to <sup>238</sup>U and that this may or may not have an impact on risk depending on the radionuclide inventory, half-life and the characteristics of the site.

Progress has been in addressing some of the uncertainties that were identified at that time, in particular in understanding near-field colloid populations.

As noted in the preceding sections, most available information refers to cement colloids, and those mainly from the backfill, rather than from the waste forms or containers. With this in mind, if it can be assumed that these are representative of the near-field colloid 'mix' (i.e. a more representative spectrum of colloids from all sources in the near field – cf. Figure 1.3), then it seems likely that colloids will not make a significant impact on the near-field behaviour of radionuclides. Compared to the data cited in Nirex 97, recent colloid studies have generally found lower colloid populations in the near field than considered at that time. These recent data are well supported by an improved conceptual understanding of the role of colloid stability in controlling colloid populations, which is based on the observed behaviour of a variety of colloid types (clays, silica, iron oxyhydroxides, cementitious) in a range of environments.

There remains a scarcity of relevant colloid sorption data. This has been circumvented in assessments by assuming that near-field (cement) colloids have surfaces that are chemically similar to the backfill cement and that differences in sorption arise from the larger specific



surface area of colloids compared to bulk cements. On this basis, colloid sorption distribution coefficients have been calculated from cement sorption data by applying an appropriate scaling factor (equation 4.1). For Nirex 97, this scaling factor was based on a single data point for uranium(VI) sorption onto colloids derived from freshly-cured NRVB. However, the cautious assumption was made that colloids generated throughout the repository lifetime would have similar sorption properties to those derived from freshly-cured NRVB. In contrast, it was considered that ageing of cement surfaces prior to radionuclide sorption may lead to a reduction in radionuclide retardation compared to that which would occur in freshly-cured NRVB. Therefore, in the assessment an ageing (reduction) factor was applied to the backfill  $K_d$ s but not to colloids.

If the recently measured (probably cautious) colloid population levels are combined with the cautious sorption distribution coefficients for near-field colloids used in Nirex 97 then, in the absence of significant concentrations of organic materials that might stabilise near-field colloid populations, there would be no significant colloid-associated radionuclide load in the near field.

There remain a number of sources of uncertainty in these simple scoping calculations, however.

- There is uncertainty concerning the potential importance of the small-sized fraction of the colloid populations between about 3 and 15-100 nm in size, which are expected to have the largest surface area to mass ratio and thus may be significant with regard to available surface sites for radionuclide sorption.
- There is little data for sorption onto near-field colloids, and it is not clear whether sorption onto fresh-NRVB derived colloids will adequately represent sorption onto the different types of colloids that may arise in a repository as a result of interactions between the cement and waste materials.
- There is uncertainty about how representative colloid populations derived from freshlycured NRVB may be of colloid populations generated from the mix of materials present in the repository over very long timescales.
- There remains uncertainty about the potential ability of wasteform-derived and natural (i.e. fulvic-like) organic compounds to enhance the stability of near-field colloids compared to concentrations that have been measured in experiments.
- There is uncertainty concerning the stability and mobility of near-field colloids on migration into the far field. In Nirex 97, on the basis of thermodynamic considerations near-field colloids were assumed to dissolve on migration into the geosphere (and release associated radionuclides into solution). However, this process has yet to be demonstrated experimentally.

These uncertainties suggest that the above calculations should be treated cautiously for the time being and that additional experimental data addressing these specific uncertainties would build confidence in the conclusions.

In addition, there remains uncertainty about the reversibility of sorption processes to colloids in general. The assessment models in Nirex 97 assumed simple, reversible, sorption of radionuclides on solid phases and colloids in both the near and far fields; evidence is now emerging that reversible sorption is not always the case for cement, and so may not be the case for near-field (or far-field) colloids.

The Nirex 97 source term model, which assumed a homogeneous well-mixed system, did not require assumptions to be made concerning the reversibility of sorption to colloids in the near-field, because no benefit was taken of the retarding effects of near-field transport processes. In the Wellenberg assessment undertaken by Nagra, transport processes were included in the near-field models and the effects of sorption reversibility could be discriminated. For a cautious colloid case assuming irreversible sorption of radionuclides to 1 ppm of colloids in the waste packages and the subsequent migration of colloid-associated radionuclide through



the near-field without retardation, the fractional release from the near-field occurred earlier, reached a peak earlier but the maximum in the flux was increased by only a factor of two compared to the colloid-unaffected case. Thus even with significant and irreversible sorption of radionuclides assumed to a high concentration of near-field colloids in waste packages, which were assumed to be mobile in the near-field, the colloid-influenced fractional release rates were of the same order of magnitude as those without colloids. The magnitude of this effect on peak release rate appears to be comparable with that on peak risk found in Nirex 97 for the colloid case without near-field organics.

Both the Nirex 97 and Wellenberg assessment calculations assumed a cautious model for near-field colloid stability and mobility. In reality, most near-field colloid types are expected to be destabilised under cementitious near-field conditions and thus have limited mobility. As noted above, irreversible or time-dependent (kinetically slow) sorption process will occur to near field solids as well as onto colloidal particles and such processes, for which no benefit is taken in PA calculations, will tend to reduce dissolved radionuclide releases from the near field. Therefore, it would appear likely that the beneficial effects of radionuclide incorporation into bulk solids (good news) would outweigh (probably significantly) the potential detrimental effects of irreversible sorption to colloidal particles (bad news) in the near field.

#### 7.3 State of development of experimental methods

In this section, the state of development of experimental methods for studying colloid populations and their stability will be summarised. A pre-requisite for the majority of the experimental work described in this report is the ability to discriminate, measure and characterise colloid populations. Developments in this area will be described in the following sub-section. Experimental methods to investigate the generation and presence of near-field colloids will then be discussed.

#### **Colloid Analysis**

- In general, number concentrations in near-field colloid populations have been found to be low, with concentrations typically of order 10<sup>10</sup> particles dm<sup>-3</sup>, and as a result are difficult to study and quantify experimentally.
- Existing data for colloid populations under near-field conditions are limited by the range of the colloid size distributions that were readily accessible to measurement. In particular, it is difficult to measure quantitatively the smallest size fractions of the size distribution, that is, in the range 1-50 nm, by conventional techniques. The minimum particle sizes measurable quantitatively, have been about 15 nm when applying TEM and about 50 nm for SEM due to constraints imposed by specimen preparation techniques (and instrument resolution in the case of SEM), particles of smaller size may also be captured by specimen preparation but not quantitatively.
- Single particle counting (SPC) techniques using particle sensors have been developed that allow rapid, direct measurement of particle size distributions on water samples without needing the lengthy intermediate specimen preparation required by electron microscopy techniques. Although, this method also has limitations in measuring the smallest particle size fraction (i.e. less than 50 nm), the potential for artefact colloid production prior to analysis is significantly reduced.
- The recently-developed laser induced breakdown detection (LIBD) technique does allow quantitative measurement of the smallest size fraction of colloid populations, and has been applied successfully to study natural colloid populations in groundwaters. The technique has yet to be applied to near-field colloids.
- All methods for characterizing colloid populations are limited by the presence of background colloid concentrations in the natural (and laboratory) environment (e.g. fine dust in air, particles in water systems) and the potential for artefact colloid formation,



which is greater the more sampling handling is required. In the case of near-field colloids, the high pH experimental systems are prone to reaction with atmospheric  $CO_2$  to precipitate calcium carbonate. This can be mitigated in the laboratory by undertaking all experimental work in nitrogen atmosphere gloveboxes and by sampling in the field using closed systems to avoid any contact of the sample with air. Nevertheless, limiting background particle concentrations of  $10^6$  to  $5 \, 10^7$  were reported by PSI when applying SPC under highly controlled conditions, for example.

 In general, it is easier to control the experimental conditions in the laboratory to minimize artefact colloid production when undertaking experiments to simulate nearfield conditions than it is when sampling natural colloid populations in groundwaters in the field.

A short overview of novel colloid analytical techniques was provided in Appendix 1. This list is not exhaustive, however, in part because of the rapid rate of development of new methods. It seems likely that this rapid rate of development will continue as the nanotechnology industry continues to boom. It is envisaged that novel methods and analytical approaches will be adopted into the more traditional environmental colloid field over the next few years. Indeed, the first re-labelling of colloids as 'nanoparticles' has begun to establish this link. Thus there is significant promise for better and more detailed characterisation of colloids (or nanoparticles) in the near future.

#### 7.3.1 Experimental Methods

As recently as 2004, an US report [116] noted that the long-term, *in situ* behaviour of cement grouts is not well understood and that cement degradation pathways are "....*still not fully understood*." and this is reflected in the colloid generation experiments reported in section 2.2, with a wide range of basic approaches employed. This makes intercomparison of the data on colloid populations and types rather complex as there are clear method-induced differences in measured colloid populations. Nevertheless, the experiments have been useful in indicating the likely orders of magnitude of colloid concentrations which will be present, so helping to evaluate the potential significance of near-field colloids.

The strengths and limitations of the main experimental methods can be summarised as follows.

#### a) Batch experiments

Batch leaching experiments can best be described as highly simplified scoping experiments that allow the potential for colloid generation from simple combinations of solid materials and simulated groundwaters to be evaluated. They are highly flexible and potentially allow a wide range of experimental parameters to be varied, such as solid to liquid ratio, temperature, salinity, solid phase composition, etc. They are relatively easy to set up and maintain and can be run for varying durations ranging from days to years, although timescales in the laboratory are inevitably short compared to those in a repository. The scale of the experiments can also be varied.

To date, batch experiments have been undertaken at relatively low solid to liquid ratios that are not representative of ratios in a repository. This does not mean that higher solid contents could not be used in principle. A pre-requisite is that sufficient leachate should be available for sampling.

With the exception of some of the very early studies of cement colloid generation undertaken by UKAEA [26], batch leaching experiments to date have been undertaken on single backfill or grout blends, although more complex solid mixtures could be used. Both granulated (crushed) and cut or moulded monolith samples have been used in colloid leaching experiments. Where crushed cements are used, the crushing process introduces a colloid generation mechanism that will not arise in a repository and this is likely to produce an over-estimate of likely colloid populations *in situ*.



Some protocols agitate the sample in a manner which would appear to be unrepresentative of near-field conditions and which may introduce a number of unrepresentative colloid generation and/or loss processes. Agitation may on one hand lead to increased particle production by erosion and disaggregation of agglomerates; on the other it may increase the tendency for orthokinetic aggregation as a result of increased frequency of particle collisions at higher kinetic energies. Settling of suspensions at the end of agitation may also lead to the removal of smaller colloidal particles that are collected by larger particulates as they sediment. Although some agitation of experiments is almost unavoidable during sampling and handling, ideally, any such agitation should be minimized.

Batch experiment have the particular advantage that they can be easily set-up, maintained and sampled within a nitrogen-atmosphere glovebox, thus minimising the potential for contact with air and high levels of CO<sub>2</sub>. Given appropriate facilities, the experimental atmosphere is relatively straightforward to control.

#### b) Column experiments

Column experiments have not been widely used to study colloid generation from cements mainly because they are much more complex to set up and run than simple batch leaching experiments. The sampling of colloids from the COLEX experiment was an example where the opportunity was taken to gain additional information on colloid generation from an existing larger scale experiment.

Compared to batch leaching studies, the solid to liquid ratio was significantly lower and more representative of the near field. However, crushed material was used and the in-column flow velocities were considerably higher than would arise in a repository, which may have enhanced colloid release by erosion. Thus enhancement of colloid concentrations would be expected compared to *in situ* conditions.

Direct comparison of the results of the COLEX colloid sampling with the PSI batch leaching experiments on M1 backfill is not possible, however, due to the different pH and composition of the cement-equilibrated waters used. Thus, it has not been possible to evaluate method-induced differences in populations between the experimental methods used at PSI.

#### c) ELTs

In contrast to simple batch leaching experiments, ELTs are much more complex to set up and run, particularly where active wastes are used or if they are operated at a larger scale. Owing to the resources required, larger-scale ELTs, which combine simulated or real waste materials and grout or backfill cements, are designed to look at a range of near-field processes (such as radioelement dissolution, rates of gas generation, evolution of chemical conditions, etc) of which colloid generation would just be one. In general, they are usually run for sufficiently long timescales to characterise the evolution of processes and chemical conditions of principal interest.

In larger-scale ELTs, higher solid to liquid ratios have been used that are more realistic, but which may still not be fully representative of the near field. Clearly, the combination of waste and cementitious materials is much more representative of the repository environment.

However, the sampling, specimen preparation and analysis of colloid populations from active tests are more complicated than from inactive experiments. In particular, the availability of facilities for characterising active colloid samples is much more limited.

For larger-scale ELTs, effective sealing of the system is important to maintain control of the atmosphere and closed sampling systems are required to avoid unwanted contact with air, which could introduce artefact colloids into the experiments.

It is recommended that characterisation of colloid populations is integrated into any future ELTs undertaken on the UK programme.

#### 7.3.2 Future approaches

#### a) Laboratory experiments

Arguably, a common experimental protocol is required for the evaluation of near-field colloid production processes [117], which should be based firmly on the conceptual models for the conditions present within the near field during its evolution.

The main uncertainties concerning possible near-field colloid populations concern the nature and stability of colloids arising from aged cements, wasteform materials and the interactions of waste components with the backfill and also the effect of waste-derived organic compounds on colloid stability. Thus in future it is envisaged that more complex experiments involving more than one solid component (e.g. grout plus a waste material) may be required to address such uncertainties.

Simple batch leaching experiments of the type undertaken previously on the Nirex programme and the 30 dm<sup>3</sup> scale combined waste ELTs represent the two extremes of leaching experiments covering a range of complexity and scale that are practicable in the laboratory. As noted previously, batch leaching tests are highly flexible and can be used to evaluate a range of potentially important parameters through scoping studies. Particular parameters of interest that may be studied using batch leaching tests include:

- higher, more realistic solid to liquid ratios;
- effect of waste loading on local colloid generation;
- longer experiment durations; and
- stabilities of colloid populations following sampling to monitor rates of aggregation and deposition under the experimental conditions.

In addition, wherever possible, future tests should make use of a range of analytical techniques that allow resolution of colloid populations over the full size range (from 1-1000 nm). In particular, the concerns about the potential contribution of the small-size colloid fraction on radionuclide transport could be addressed through a systematic filtration study using a range of pore-size filters to examine radionuclide partitioning between colloid size fractions and the solution phase in simulated near-field leachates.

The use of crushed materials and agitation of the experiments are both considered to potentially enhance colloid populations and should be avoided where realistic rather than cautious assessments of colloid populations are required. One potential improvement would be to use small volume cured cement samples suspended in the leachant solution. This would have the particular advantage that deposited solids could be recovered and analysed, which is not possible using crushed material.

Arguably ELT experiments offer the most realistic method of better assessing the true *in situ* conditions in a repository near field. If such complex, costly and long-term experiments are to be repeated, the opportunity should be taken to optimise the design to more accurately reflect the *in situ* conditions, including such aspects as solid to liquid ratios, etc. It could be argued that such work should wait on the definitive design for the UK cementitious repository, but this overlooks the fact that carrying out an improved ELT experiment will provide the basic mechanistic understanding which will be required, regardless of the design specifics. Areas where improvements could be made include:

• the S:L ratio – ideally as representative as possible;



- the materials mix must reflect the repository reality (cf. Figure 1.3);
- no agitation of the system is allowed this has no relevance to a deep, geological repository;
- experimental timescales must be realistic (i.e. decades, rather than months to years);
- a 'hot' experiment would be preferable, especially when focused on radionuclides of direct PA relevance;
- specific evaluation of microbes and organics ; and
- where possible, integrate the project with other long-term assessments (see discussion in [270]) such as URL experiments (comparison of spatial scales) and natural analogue studies (comparison of temporal scales).

Advances in analytical techniques over the last 10 years since the previous experiments were carried out mean that the S:L ratio could be made much more realistic. Micro-, in-line and element-specific electrode methods could cut the sample volume required drastically. Additionally, advances in radiochemical methods also mean that smaller samples are required and, more importantly, improvements in detection limits mean that solubility controlled levels in the near field could be realistically recreated (cf. discussion in [63]).

In summary, current experimental formats seem likely to maximise any near-field colloid populations, which is arguably conservative. While it is accepted that differences in repository design make highly realistic experiments difficult, it also needs to be accepted that any future experiments need to more accurately reflect the true *in situ* conditions of a cementitious near field. For example, the experimental solid:liquid ratios should be more realistic, even if this makes the experiments more difficult to conduct. Likewise with agitation and mixing: rather than trying to set a protocol which would be used by all, it would appear better to omit such physical agitation altogether.

#### b) Integrated long-term experiments

As noted previously, the main limitation of most laboratory based assessment of near-field colloids carried out to support PA is the time frame. There are three possible ways of supporting these short-term experiments, so increasing confidence in the laboratory data. The first is long-term ELT experiments and these have been discussed above. The second is natural analogues and the third is long-term experiments in underground research laboratories (URLs).

#### Natural analogues

Data are currently available from only one natural analogue study, namely from examination of the Maqarin site in Jordan. The main points arising from the studies at Maqarin to date can be summarised as follows.

- The Maqarin colloid data set is unique, so it is hard to compare it directly with any existing laboratory data (especially keeping in mind the comments on intercomparison of laboratory data in sub-section 7.3.1).
- Maqarin is directly representative of a surface to near-surface repository in a high permeability host rock (with a high energy flow system), but can be used to assess a geological system in a qualitative manner [cf. 121].
- The site represents fractured cement; the natural cement is an aquaclude (i.e. it is highly impermeable).
- The data from Maqarin indicate that the cementitious colloids are stable in alkaline waters; however the behaviour of colloid populations across interaction fronts has not been investigated.



- An attempt was made to study the reversibility of sorption onto cementitious colloids by uranium-series isotope (disequilibrium) method. This approach was employed on the colloids sampled at the Eastern Springs site at Maqarin, but the amount of uranium associated with these colloids was below the detection limit of the equipment then available (over a decade ago). Improvements in analytical techniques imply that it may be worth repeating the exercise.
- Organic material appears to be deposited, along with secondary calcite, within the rock matrix in the ADZ and this might be worth further study at both the Maqarin and Khushaym Matruk sites (see [121] for details) to establish if this retardation of organics is of relevance to a repository.

Future work at Maqarin will focus on the surviving site, the Western Springs. Unfortunately, the Eastern Springs site where the cement colloid samples were collected has been effectively destroyed by construction of a new joint Jordanian-Syrian-Israeli reservoir and hydro-scheme. The Western Springs site is downstream of the dam and remains in pristine condition.

Two natural analogue sites for low-alkalinity cementitious systems have been described recently in the Philippines [118]. Current studies are looking at the impact of cement-like leachates on the host rock and bentonite. These sites are more directly relevant to repository concepts where low-pH cements are under consideration as backfill materials and the repository may be surrounded by a bentonite buffer (such as in Japan), rather than to high-pH repository concepts such as that developed in the UK.

No data are yet available on colloids from these sites. The current understanding of the flow system is such that, in addition to bentonite/alkaline groundwater interaction [271], it may be possible to examine changes in cement colloids as they cross interaction fronts (see comments on Magarin, above) downstream from their source in the future.

#### URL experiments

Currently, there is a long-term URL study of cementitious systems of relevance to near-field colloids in progress. This is the Long-term Cement Studies or LCS experiments at in the Grimsel Test site in Switzerland (see Figure 7.1). The project is planned to run for at least a decade and potentially up to 50 years (see [269]). The current plans include study of:

- changes in the sorption behaviour of actinides (or homologues) within the ADZ;
- the influence of organic material (e.g. complexation, degradation), in particular the behaviour of superplasticisers used in low pH cement;
- the presence and mobility of microbes and colloids in the ADZ; and
- bentonite-cement interactions.

All of these topics are of direct relevance to the behaviour of near-field colloids.

#### 7.4 State of development of modelling approaches and treatment in PA

#### 7.4.1 Modelling approaches

In general, the majority of work considered in this review has been concerned with experimental studies of colloid presence, stability and the association of radionuclides with colloids. The main area of modelling of colloid behaviour considered in this report has been the understanding of colloid stability and prediction of colloid aggregation behaviour.



The long-standing DLVO theory of colloid stability provides a sound basis for the semiquantitative understanding of colloid stability behaviour. In particular, the theory has provided a qualitative basis for understanding the role of colloid stability in controlling colloid populations in a wide range of groundwater systems and provides a qualitative explanation for differences in colloid populations measured in leaching experiments with HFSC. The theory does have quantitative 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, therefore rates of colloid aggregation need to be measured.

A number of other areas of the modelling have not been covered in detail, including: the mathematical description of colloid populations; modelling of sorption onto colloids; colloid transport; and modelling of the ADZ.



Figure 7.1 Planned experimental layout of the LCS experiment: the basic experimental concept foresees emplacement of cementitious material through injection boreholes from the tunnel (centre) into the fully saturated water conducting shear zone (grey plane intersected by the tunnel). The natural groundwater flow is radially towards the tunnel wall so sampling boreholes will be drilled between the source zone and the tunnel to 'capture' the alkaline flow. Image courtesy of Nagra



Some work on the mathematic description of colloid populations has been undertaken in Switzerland and is described in references [9 and 55].

Given the sparsity of data for radionuclide association with near-field colloids, no studies of thermodynamic modelling of radionuclide sorption onto near-field colloids have been published. In general, it is assumed that the sorption processes occurring at the surfaces of colloids will be similar to those occurring on bulk solid surfaces and that similar thermodynamic sorption models can be applied. Attempts have been made to calculate the surface areas available for radioelement sorption onto colloidal populations based on measured particle size distributions [e.g. 55]. However, such models generally rely on the approximation that the particles are hard spheres with surface area proportional to the radius squared. In practice, near-field colloidal particles have been observed in a variety of shapes (spheroids, rods, flakes) and may be composed of aggregates; larger particles may possess integranular porosity. Thus the hard-sphere model may be over-simplified, as recognised in [55]. In general, the relationship between the available surface area (i.e. available concentration of sorption sites per unit mass) and particle size for near-field colloids has yet to be clearly established.

Owing to the low stability of colloids expected under near-field conditions, no requirement to model colloid transport by the groundwater pathway in the near field or the ADZ is foreseen in the immediate future. Therefore no attempt has been made in this study to review recent developments in colloid transport modelling. This is a mature topic with a considerable body of literature.

Understanding of the ADZ has improved considerably over the last decade since Nirex 97 due to focused laboratory studies [e.g. 272], further investigations at the Maqarin natural analogue site [e.g.121] and improved modelling capabilities [e.g. 273]. However, a detailed, mechanistic understanding of the processes that will affect colloids (whether they are near-field colloids leaving the repository or far-field colloids entering the repository) has yet to be developed. Work is ongoing on international programmes to develop thermodynamic and reactive transport models for the chemistry of the ADZ to assist the interpretation of laboratory data. An understanding of solute behaviour is required to develop conceptual models for colloid behaviour in the ADZ. In the reactive zones of the plume where dissolution and re-precipitation processes are occurring, there is particular potential for the co-precipitation of radioelements into new phases and the incorporation of radionuclides into colloids and bulk solids. A better understanding of such processes and an evaluation of the potential impact of radionuclides irreversibly sorbed onto near-field colloids would be particularly valuable.

#### 7.4.2 Treatment of near-field colloids in PA

To date, there have been two main approaches:

- bottom-up, driven by a detailed laboratory programme (e.g. in the UK and Japan)
- top-down, driven by the perceived requirements of the repository PA (e.g. Belgium and Switzerland)

These assessments differed in their objectives and the levels of detail in which colloids were treated vary significantly. The Nirex 97 and Wellenberg [83] assessments were major PAs undertaken in the mid-1990s in which the potential impact of colloids was treated specifically in reference and/or variant calculations. The more recent SAFIR-2 (2001) [244] and TRU-2 (2007) [17] assessments are reports on the state-of-the-art on radioactive waste disposal in their respective national programmes, rather than detailed assessments. In both SAFIR-2 and the Project Opalinus Clay assessment (2003) [79], the discussion of colloids is limited to FEP analysis and most of the near-field colloid FEPs were screened out at an early stage of the assessment process. In both assessments, this is because the high isolation properties of the repository host rock (a plastic and an indurated clay, respectively) mean that most near-field processes can rapidly be screened out as non-significant.



There are clear implications here if any future UK repository site host rock were shown to have similar isolation qualities, but such screening out of near-field processes is not currently an option.

The methodology for treating colloids in the Nirex 97 assessment (as outlined in sub-section 6.2.2) was based on the representation of the disposal system developed for the assessment and the structure of the models incorporated into the assessment code (MASCOT). Additional processes affecting the colloid-facilitated transport of radionuclides may need to be considered in future assessments if more complex models for parts of the disposal systems are developed. In other words, more detailed consideration may need to be given to near-field colloid FEPs and simple scoping models developed for scoping purposes.

The near-field models used in Nirex 97 and in the most recently published Nirex generic performance assessment, GPA03 [245] (SLST models), make no attempt to account for physical barriers and transport processes within the near field. The near field vaults are assumed to be homogeneous well-mixed systems. For the treatment of colloids in Nirex 97 (colloids were not treated in GPA03) the assumption was made that near-field colloids are uniformly distributed in the flowing porosity. Although sorption onto colloids was treated as a reversible, equilibrium process, in fact the assumption of sorption reversibility was unnecessary in this case.

The treatment of colloids in the Nirex 97 SLST models appears to provide an appropriately cautious method for scoping the potential impact of near-field colloids on the source term of a GDF. Only if such scoping calculations indicate that the impact of the near-field colloid population is potentially significant would more detailed treatment of colloids be justified.

The authors understand that the near-field model is currently under development for future NDA RWMD assessments.

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## 8 Conclusions

The main conclusions from this study are as follows.

- Experimental work carried out over the last ten years has found that cementitious colloid populations derived from a variety of potential cementitious backfill materials under simulated near-field conditions are low. Colloid populations are smaller than those on which the Nirex 97 assessment of a cementitious repository was based. There is a concern, however, about the potential importance of the smaller-sized fraction of the colloid populations, which are not readily accessible to measurement with traditional colloid characterisation techniques. These are expected to have the largest surface area to mass ratio and thus may be significant with regard to available surface sites for radionuclide sorption. In general, the effects of the smallest sized particles (1-3 nm) are taken into account in near-field solubilities which are defined by the use of 30,000 NMWCO filters in solubility experiments. The remaining size gap could be addressed by a systematic filtration study of radionuclide partitioning between different colloidal size fractions in simulated near-field leachates.
- There is a growing body of evidence that colloid populations in environmental systems with low organic concentrations are controlled by the ionic strength of the water, which controls the rate of particle aggregation. The high calcium concentrations in a cementitious near field are expected to destabilise colloids leading to particle aggregation and sedimentation or deposition onto surfaces. As a result, in the absence of significant interaction with organic materials, colloid populations in the near field are expected to be controlled to low levels by the chemical conditions.
- Association of inorganic particles with natural organic compounds is an important mechanism for colloid stabilisation in surface and near-surface waters, where concentrations of natural organic materials may be high. Due to the large amount of organic materials in the UK waste inventory, this mechanism could potentially operate to stabilise and enhance colloid populations in the near-field porewater. Limited experimental evidence to date does not support this contention, however, although this remains an area of uncertainty. Natural, low molecular weight organic materials (fulvic acids), that are alkaline-soluble, may also enter and be stable in the near field; their potential impact on near-field colloid populations (and as complexants of radionuclides) will be a site-specific issue.
- On thermodynamic grounds, cementitious colloids are not expected to be chemically stable but to dissolve on migration from the high pH near field to the low 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.
- There is a lack of published data for sorption of radioelements onto near-field colloids. Only one data point is currently available. Further data would assist in building confidence in the understanding of radionuclide sorption to cementitious near-field colloids.
- Two cases are often considered when treating colloid-facilitated transport of radionuclides in performance assessment: reversible and irreversible sorption of radionuclides onto colloids. At the levels of colloid concentrations measured in experiments and cautious values for sorption distribution coefficients onto colloids, the case of reversible sorption to colloids is not thought to be an issue for repository safety.
- There is uncertainty concerning the reversibility of sorption processes to colloids in general. The treatment of near-field colloids developed for the Nirex 97 assessment, in which the near field is treated as a homogeneous well-mixed system with a uniform distribution of stable and mobile colloids in the transport porosity, requires no assumptions to be made concerning the reversibility of radionuclide uptake to colloids. Thus the approach provides a suitably cautious method for scoping the impact of



colloids in the near field on the source term that includes the irreversible sorption case to mobile colloids. Only if such scoping calculations indicate that the impact of the near-field colloid population is potentially significant would consideration of colloids in more complex near-field models be justified.

- In the Nirex 97 assessment, it was found that colloids present in the near field could have an impact on the source term and increase risk from <sup>238</sup>U daughters at long times should the situation arise that organic complexants are effectively removed from the near field. However, if recently measured colloid populations levels are combined with the cautious sorption distribution coefficients for near-field colloids and in the absence of significant concentrations of organic materials, then there would be no significant colloid-associated radionuclide load in the near field. Given the uncertainties noted above, this conclusion should be treated cautiously for the time being; additional experimental data addressing these specific uncertainties would build confidence in this conclusion.
- If sorption to colloids is found to show significant irreversibility and colloid particles are found to persist then there may be a need to develop further understanding of colloid mobility and chemical stability in the near field and into the far field. However, the same processes by which radionuclides may be irreversibly sorbed to colloids are also likely to occur at the surfaces of cements and rock. In reality, given that near-field colloids are expected to have limited persistence (i.e. finite lifetimes) in the geosphere, the effects of radionuclide retardation by immobilisation with solid phases are likely to outweigh the detrimental effects of transport of radionuclide irreversibly bound to near-field colloids.
- The association of particles (including larger particulates) with the surfaces of gas bubbles (flotation) or droplets of LNAPLs may provide mechanisms for particle transport out of the near field by buoyancy-driven flow. Owing to uncertainties concerning the impact of gas transport and the formation and transport of NAPLs in a repository, assessment of the significance of flotation and LNAPLs-associated particle transport does not yet seem appropriate.

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## Appendix I New Frontiers in Colloid Characterisation

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#### A1.1 Introduction

As discussed in Section 2.2, a range of analytical methods have been applied to study the concentrations, compositions and particle size distributions of colloidal particles in environmental and simulated near-field samples, including:

- transmission electron microscopy (TEM) coupled with energy dispersive X-ray analysis (EDX);
- scanning electron microscopy (SEM) coupled with EDX;
- photon correlation spectroscopy (PCS, or dynamic light scattering); and
- single particle counting.

As indicated in Section 2.2, these techniques are continually undergoing developments with improvements in resolution, turn-around time, degree of automation, data/image quality and ease of handling, etc. In recent years, a number of new techniques have been developed specifically for the examination of groundwater colloids, which may also be applicable to the study of near-field colloids. These include:

- laser-induced breakdown detection; and
- single particle inductively-coupled plasma-mass spectrometry (SP ICP-MS).

Heightened interest in nano-technology has spurred increased investment in analytical techniques that can characterise and manipulate materials at colloid-relevant scales. Consequently, several of these novel techniques which have found widespread application outwith the traditional colloid community are reaching the point where they could be of relevance to colloid science in general and in colloids in waste disposal in particular. Indeed, the use of the term 'nano-particle' rather than 'colloid' (e.g. [A1]) may be a first sign of this cross-over. Two such techniques are:

- environmental SEM (ESEM); and
- focused ion beam (FIB) microscopy.

In addition continued advances in synchrotron-radiation based techniques, built around the development of high-intensity 4<sup>th</sup> generation synchrotron radiation sources, such Diamond at Harwell in the UK, are opening up new opportunities for studying the compositions of natural colloidal materials and the mechanisms of association of radioelements with inorganic and organic colloidal particles using:

• X-ray absorption spectroscopy (XAS).

In this Appendix, some of these new techniques, which may of value in any future colloid experimental programmes, are briefly discussed. The interested reader is referred to the specific references cited for more detailed information.

#### A1.2 Laser-induced Breakdown Detection

Laser-induced Breakdown Detection (LIBD) was developed to fill a gap in the ability of conventional colloid characterisation techniques to study the smallest size fractions of colloid particle concentrations (i.e. <20-50 nm, depending on the techniques being applied).



LIBD is based on the generation of the dielectric breakdown of water in the focus region of a pulsed laser [A2]. In the system developed by FZK-INE in Germany, a pulsed beam (frequency 15 Hz at 532 mm wavelength, with pulse energies typically under 1 mJ and pulse lengths of several ns) from a Nd-YAG laser is passed through a variable attenuator and a beam splitter and then focussed on the centre of a flow-through cell. As a result of the very high electrical field strength (around 10<sup>11</sup> Vm<sup>-1</sup>) the electrons are released by multi-photon absorption. The initially released electrons absorb further light quanta and are accelerated within the electrical field of the laser pulse. These electrons in turn knock further electrons out of atoms which in the end leads to an electron avalanche and the resultant increase in ionisation generates a plasma. The rapid expansion of the plasma generates a shock wave. At the end of the laser pulse the plasma cools down, recombination processes occur and light is emitted.



### Figure A1.1 FZK-IME's LIBD fits in the back of a van and can be driven directly on-site for analysis (from [A3])

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 laser beam exceeds that for colloids. An piezoelectric transducer monitors the cell for breakdown shockwaves and a camera records the plasma light emissions. The spatial distribution of several thousand plasma emissions recorded within the focal volume indicates the mean colloid diameter. The evaluation of the number of breakdown events per number of laser pulses results in a breakdown probability and this, along with the colloid diameter is used to calculate the colloid concentration. Colloid



populations are given relative to a calibration with polystyrene reference colloids. Compared to conventional laser light scattering methods, LIBD is approximately 6 orders of magnitude more sensitive for particles smaller than ~0.05  $\mu$ m

Recently, FZK-INE have developed a mobile version of their LIBD (Figure A1.1) and this has been employed extensively in both Nagra's Grimsel Test Site in Switzerland [A4] and SKB's Aspö URL in Sweden [A5].

#### A1.3 Single Particle ICP-MS

A recent development at PSI, has seen the use of inductively coupled plasma - mass spectrometry (ICP-MS) to perform single particle analysis on model colloidal systems [A6,A7]. In the ICP-MS technique, transient signals induced by the flash of ions due to the ionisation of a colloidal particle in the plasma torch can be detected and measured for selected ion masses by the mass spectrometer. The size of the signal is directly proportional to the isotope mass in each particle. The signals recorded via time scanning (typically in 10 ms intervals) can be analysed as a function of particle size, to obtain a size distribution, or the fraction of the studied isotope or element in the colloid phase. The frequency of the flashes is directly proportional to the concentration of particles in the colloidal dispersion.

The PSI team have made the following comparison of the analytical performance of the technique compared to SEM and single particle counting (SPC) [A8]:

- SEM allows chemical analysis (colloid sizes > 500 nm and morphological analysis (colloid sizes > 50 nm in approximately 20 hours.
- SPC allows colloid counting (> 30 nm) in only 20 minutes.
- ICP-MS allows colloid analysis isotope by isotope for colloid sizes in the range >50-100 nm with a classic plasma torch in just 20 seconds.

This novel application of a well-established and widely available analytical technique clearly has significant potential for the study of near-field colloid particles in any future programme.

#### A1.4 Environmental SEM (ESEM)

One disadvantage of the traditional SEM is that it is normally not possible to examine samples that produce any significant amount of vapour when placed in a vacuum. This means that the samples must be dried (and usually gold coated) before analysis and this can lead to destruction of colloidal samples. The ESEM retains all of the performance advantages of a conventional SEM, but removes the high vacuum constraint on the sample environment.

ESEM is specifically designed to study wet, oil bearing, or insulating materials. Polymers, biological cells, plants, soil bacteria, concrete, wood, asphalt and liquid suspensions (e.g. colloids) have been observed in the ESEM without prior specimen preparation or gold coating. Samples may be examined in water vapour or under atmospheres such as  $CO_2$  or  $N_2$  at near atmospheric pressures due to the vacuum system of the ESEM.

The primary electron beam hits the specimen (Figure A1.2) which causes the specimen to emit secondary electrons. The electrons are attracted to the positively charged detector electrode. As they travel through the gaseous environment, collisions between the secondary electrons and atoms of gas result in the emission of more electrons and ionisation of the gas. This increase in the number of electrons present effectively amplifies the original secondary electron signal. The



positively charged gas ions are attracted to the negatively biased specimen and offset charging effects (so obviating the need for any sample coating).



Figure A1.2 Principal behind ESEM (courtesy Michigan State University)

If a large number of electrons is emitted from a position on the specimen during a scan, there is a strong signal, but if only a small amount of electrons are emitted, the signal is less intense. The difference in signal intensity from different locations on the specimen allows an image to be formed. Generally, however, better resolution is obtained at lower (i.e. 85-90% relative humidity).

To date, ESEM has been used to better assess *in situ* colloid morphology [A9] (but note the resolution constraint noted above), to directly study attachment of colloids to fracture faces and pore surfaces (e.g. [A10]) and to examine organic colloids (e.g. [A11]) but has been little used in NF colloid studies to date.

#### A1.5 Focused Ion-Beam (FIB) Microscopy

The FIB microscope has gained popularity in material studies laboratories in recent years because it offers high-resolution imaging and the possibility of micro-machining with the same instrument. The FIB microscope is similar to a SEM but uses an ion-beam to raster over samples, rather than the electron beam of the SEM. The secondary electrons generated from the sample by the ion beam can be used to obtain high spatial resolution images and combined FIB-SEM instruments are now becoming the norm. FIB instruments are also commonly used for TEM sample preparation, microstructural analysis and nanomachining.

Although ion beams are not as finely focused as the SEM's electron beam, the contrast mechanisms are different and so the FIB can provide complementary information about sample surfaces. In addition, FIB can often be used to image the uncoated samples which are difficult to image by even low-voltage SEM, providing the possibility to image colloids (note the imaging resolution is currently around 10nm [A12])

Perhaps the area of greatest potential in colloid studies is the ability of FIB microscopes to produce 3-dimensional images and chemical spatial distribution in samples in the 10 nm to 1  $\mu$ m size range. The FIB can focus ions on spot sizes of the order of 5-20 nm and can produce



average serial sectioning depths of 10-15 nm (e.g. [A13]). In addition, FIB can be incorporated with a wide range of high resolution imaging and surface analysis methods (e.g. backscattered electron imaging, Auger spectroscopy, SIMS, etc) to provide even greater flexibility in sample characterisation.

If there is one significant drawback of FIB, it is that imaging can be very time-consuming and it is probably this factor which has mitigated against the use of this technique in colliod studies to date.

#### A1.6 X-ray absorption spectroscopy (XAS)

XAS uses X-rays to probe the element specific local structure of a sample. At discrete energies, characteristic of the different elements, the X-ray absorption spectrum of a material shows sharp jumps in absorption coefficient, termed absorption edges. These occur at energies where incident X-rays have sufficient energy to knock a core electron out of an atom (photoelectron emission). As shown in Figure A1.3 two distinct regions of X-ray absorption spectrum at the absorption edge can be distinguished: XANES and EXAFS. The information available from each region of the spectrum is outlined in the sections below.





#### A1.6.1 Extended X-ray Absorption Fine Structure (EXAFS)

EXAFS refers to oscillations of the X-ray absorption coefficient on the high-energy side of an X-ray absorption edge, which may extend up to 1000eV above the edge [A14]. EXAFS arise from the sensitivity of the final energy state of the emitted photoelectron to the local atomic environment of the X-ray absorbing atom (Figure A1.4). With the development of synchrotron radiation sources since the 1970s, providing high intensity tuneable X-ray sources, EXAFS spectroscopy has developed as a powerful tool for probing the short-range structure of materials. EXAFS contains information about the number, type and distance of neighbouring



atoms within one to three co-ordination shells about the chosen atom and is equally applicable to samples in solid or liquid form. EXAFS is an atom-specific method which can be used to study the local structure about one specific element within a matrix at relatively low concentration. Thus the technique is ideally suited for the study of sorbed species at mineral surfaces *in situ*.



# Figure A1.4 Schematic diagram illustrating the absorption of an X-ray photon by the central atom (dark circle) and the emitted core electron which propagates as a spherical wave (full line). Neighbouring atoms (light circles) backscatter the photoelectron wave (dashed lines) and interference at the central atom gives rise to EXAFS

The information obtainable from an EXAFS experiment depends on the short range order of the structure being investigated (and the quality of the EXAFS data); this information is obtained by model fitting to the EXAFS data. In principle, interatomic distances can be measured with good accuracy ( $\pm 0.02$  Å). The type of neighbouring atoms can be distinguished in broad terms, i.e. light atoms, such as O or C, can be distinguished from metal atoms, although knowledge of the sample is essential for data analysis and interpretation. Co-ordination numbers, which depend upon the EXAFS amplitude, can be obtained to  $\pm 20\%$  under favourable conditions. The amplitude of the EXAFS falls away with reciprocal squared of the interatomic distance which limits the number of co-ordination shells detectable about the central atom. Furthermore, the amplitude is damped by thermal and static disorder. Thus, in studies of hydrated metal ions in solution only the primary hydration (oxygen) sheath about the metal atoms can be detected, whereas studies of crystalline salts generally provide structural data on first, second and sometimes third shells.

EXAFS has been widely used over the last 20 years to study the structure of species sorbed on mineral surfaces (e.g. [A15,A16,A17],A18]). An important criterion for applying the technique is that samples contain sufficient concentrations of the element of interest so that data of suitable quality for structural analysis can be obtained. For this reason many studies have made use of minerals in colloidal form to maximise the surface are available for sorbate loading (e.g. [A19]). However, significant improvements in the quality of data obtainable on samples containing low concentrations of the target atom have been made over the last 10 years with the use of brighter synchrotron radiation sources, such as the ESRF at Grenoble and the micro-XAS line at PSI (Figure A1.5), and improvements in the performance and numbers of energy-discriminating fluorescence detectors that are used.

To date, several studies of the behaviour of radionuclides associated with groundwater colloids have been carried out using EXAFS (e.g. [A20]). The technique has also been applied to



studies of cementitious systems (e.g. [A21]). Clearly, there may be potential for applying EXAFS to determine radionuclide association with near-field colloids in the future.



Figure A1.5 A schematic illustration of the micro-XAS beamline at the Paul Scherrer Institute (PSI) in Switzerland. Besides the Pb shielded hutches (optical (A) and experimental hutch (B)), the drawing shows the outline of the control hutch (C-E) and the FEMTO laboratory (F). Image courtesy of PSI

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