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Synthesis report: Colloids and related issues in the long term safety case

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Abstract

The BELBaR project was a collaborative project based on the desire to improve the long-term safety assessments for geological disposal facility concepts for spent fuel/high level waste that combine a clay engineered barrier system (EBS) with a fractured rock.

Colloids may be mobile in groundwater and are thus potentially significant for safety because they have been shown to be able to sorb radionuclides and increase their effective concentration in groundwater above that which would be transported in dissolved form.

The main aim of the BELBaR project was to increase the knowledge and reduce uncertainties with respect to the processes that control clay colloid generation, stability and their ability to transport radionuclides and reduce uncertainties in the description of the effect of clay colloids in long-term performance assessments.

A reduction of uncertainties in the understanding may lead to:

- A reduction of the assessed overall risk from a repository.
- The possibility to totally neglect the colloidal processes in assessments under some circumstances.
- Guidance to future site selection and site characterisation programmes.
- Guidance in the selection of engineered barriers for a nuclear waste repository.

This report provides a synthesis of the progress that has been made as a result of the work undertaken within the BELBaR project along with recommendations for the potential to review the treatment of colloids in performance assessment.

Sammanfattning

BELBaR-projektet var ett samarbetsprojekt baserat på viljan om att förbättra de långsiktiga säkerhetsbedömningarna för geologiska slutförvarskoncept för använt bränsle/högaktivt avfall vilka kombinerar en ingenjörsbarriär konstruerad av lera (EBS) med en ett sprickigt berg.

Kolloider kan vara mobila i grundvatten och är därmed potentiellt signifikanta för den långsiktiga säkerheten, eftersom de har visat sig kunna sorbera radionuklider och öka deras effektiva koncentration i grundvatten utöver den mängd som skulle transporteras i upplöst form.

Huvudsyftet med BELBaR-projektet var att öka kunskapen och minska osäkerheten med avseende på de processer som kontrollerar lerkolloidgenerering, stabilitet och deras förmåga att transportera radionuklider samt att minska osäkerheten i beskrivningen av effekt lerkolloider i bedömningar av långsikt säkerhet.

En minskning av osäkerheter i förståelsen kan leda till:

- En minskning av den bedömda totala risken från ett förvar.
- Möjligheten att helt och hållet försumma de kolloidala processerna i analyserna, i alla fall under vissa betingelser.
- Vägledning till framtida platsval och forskningsprogram.
- Vägledning vid val av tekniska barriärer för ett kärnavfallsförvar.

Denna rapport ger en sammanfattning av de framsteg som gjorts till följd av det arbete som utförts inom BELBaR-projektet tillsammans med rekommendationer för möjligheten att förbättra hanteringen av kolloider i framtida säkerhetsanalyser.

Acknowledgement

This report is a product of Work Package 1 of the BELBaR project. All participating organisations and personnel are thanked for their significant input that determined its structure and contents, and for associated texts that collectively make this report.

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Contents

1 Introduction

The BELBaR project was a collaborative project based on the desire to improve the long-term safety assessments for geological disposal facility concepts for spent fuel/high level waste that combine a clay engineered barrier system (EBS) with a fractured rock. BELBaR partners included national radioactive waste management organisations (WMOs) from a number of countries, research institutes, universities and commercial organisations working in the radioactive waste disposal field.

The formation and stability of colloids from the EBS may have a direct impact on assessed risk from a geological disposal facility in two aspects;

- generation of colloids may degrade the engineered barrier; and
- colloid transport of radionuclides may reduce the efficiency of the natural barrier.

In this project the terms "colloid" or "colloids" are used primarily to denote the clay particles rather than the phase. The term in general, however, is commonly used to denote the phase/mixture (e.g. mayonnaise is a colloid). The term "colloid" can, however, also be used to specifically denote the individual particle. However, in some respects in this project, especially concerning colloid stability the term has been used for the phase.

An increased understanding of the processes involved in the above aspects will have a significant impact on the outcome of future assessments. Therefore, the main aim of the BELBaR project was to increase the knowledge of the processes that control clay colloid generation, stability and their ability to transport radionuclides and reduce the uncertainties in the description of the effect of clay colloids in long-term performance assessments. To meet this aim, a number of experimental and modelling activities were undertaken within the project.

The primary target audience of the outcome of the project is national WMOs. The key use will be increased understanding of processes that have been shown to have a direct impact on the assessed dose/risk from disposal facilities for high-level radioactive waste or spent nuclear fuel.

2 Structure of the project

The BELBaR project was organised into a number of work packages. The structure and objectives of these work packages are discussed in the following sub-sections.

2.1 WP1: Safety assessment (RWM[1] lead)

The objectives of WP1 at the outset of the BELBaR project were to identify and synthesise the current treatment of the relevant processes in existing safety assessments. This review was used to inform the direction of the experimental and modelling programme undertaken within the framework of the BELBaR project.

At the end of the BELBaR project, the objective of WP1 was, by drawing on the results obtained within the respective work packages (as illustrated in Figure 2-1), to consider and where appropriate, to recommend opportunities for where WMOs could review how colloids and related phenomena are considered in the long-term safety case.

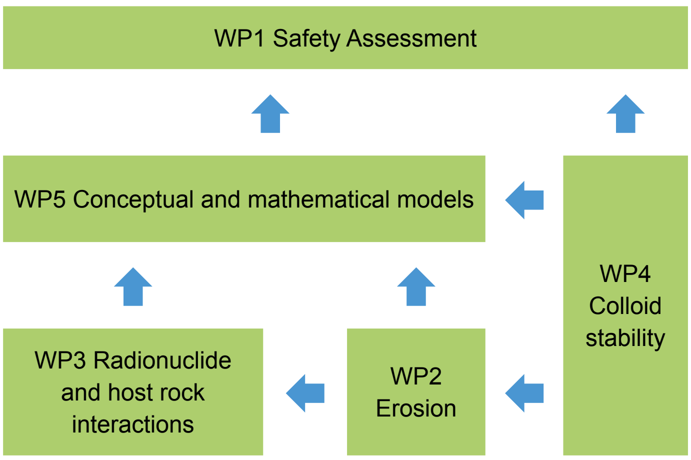

Figure 2-1. *Information flow from BELBaR WP2-5 into WP1.*

2.2 WP2: Bentonite erosion (Ciemat lead)

The main objective of WP 2 was to understand the main mechanisms of erosion of clay particles from the bentonite surface and to quantify the (maximum) extent of the possible erosion under different physico-chemical conditions.

2.3 WP3: Radionuclide and host rock interactions (KIT lead)

The objective of WP3 was to develop process level understanding of colloid mobility controlling processes and their appropriate description. This included radionuclide sorption and retention processes.

[1] Radioactive Waste Management (RWM), a wholly owned subsidiary of the Nuclear Decommissioning Authority (NDA) was previously known as the Radioactive Waste Management Directorate (RWMD).

2.4 WP4: Colloid stability (ÚJV Řež lead)

The objective of WP4 was to understand clay colloid stability under different geochemical conditions with respect to ionic strength, pH and the influence of complexing agents (organic/humic substances).

2.5 WP5: Conceptual and mathematical models (Posiva lead)

The objective of WP5 was to validate and advance the conceptual and mathematical models used to predict mass loss of clay in dilute waters and clay colloid generation as well as clay colloid-facilitated radionuclide transport relevant to geological disposal of high-level radioactive waste and spent nuclear fuel.

2.6 WP6: Knowledge management, dissemination and training (SKB lead)

To ensure that BELBaR had the appropriate impacts, a specific work package was established for dissemination of results. BELBaR has utilised a number of avenues to disseminate knowledge including; the project website providing the primary initial interface for partners and the wider scientific community, project meetings, reports, workshops, journal publications, presentation at international conferences and training through a project coordinated professional development course.

2.7 WP7: Coordination (SKB lead)

The objective of WP7 was to provide adequate administrative, legal and financial management of the project, and documentation of scientific-technical progress through Annual Workshop Proceedings to ensure the overall function of the project work and activities.

Work Packages 6 and 7 are not discussed further in this report.

3 Structure of this report

In Section 4, a summary of how each of the waste management organisations participating in BELBaR currently considers colloids in performance assessment is presented. This represented the state-of-the-art at the outset of the project.

Section 5, provides a synthesis of the issues identified at the start of the BELBaR project and on which the experimental and modelling work within the work packages was developed. Progress against these issues made throughout the course of the BELBaR project is presented, providing a demonstration of the benefit that the BELBaR project has brought to the national programmes participating in the project, with respect to the treatment of colloids in performance assessment.

Section 6, provides a summary and further recommendations based on the conclusions of Section 5.

4 Summary of the current treatment of colloids in performance assessment

At the outset of the BELBaR project, a State-of-the-art report was produced on the treatment of colloids and related issues in the safety assessment (Beard et al. 2012). This report captured the limitations and uncertainties associated with the existing treatment and identified needs for additional studies of colloidal behaviour to be addressed in the BELBaR project. A summary of the treatment of colloids as reported by the participating WMOs (Posiva (Finland), SKB (Sweden) and RWM (UK)) is given below.

4.1 Finland

Colloids have received little attention in performance assessments to date. It has been the general idea that colloid facilitated radionuclide transport has only diminutive effects on safety. In summary:

- The occurrence of deionised groundwater conditions within the buffer and backfill has not been excluded and therefore groundwater is assumed to be deionised at the repository level.
- Since currently, the full scale numerical model, used in performance assessments prior to BELBaR, can only deal with monovalent systems, all exchanger sites in clay components are assumed to be occupied with Na^+ ions.
- Mass loss rate is assumed to scale with groundwater flow velocity (u) as $u^{0.41}$ since validation of a new model is pending and thus pessimistic values are chosen for the estimate of number of canister positions with advective conditions.
- It is assumed that fracture aperture scales with fracture transmissivity as $2b_v = 10 \times 0.0117 \times T^{0.33}$
- The formation of accessory mineral bed layers during erosion of bentonite is neglected since, although there are indications of such a process, only limited qualitative evidence exists.
- It is assumed that erosion will be significant only in a few locations within the repository.
- It is assumed that the radiological consequences of colloid-facilitated transport are small (Nykyri et al. 2008).

4.2 Sweden

In SR-Site, for situations where the groundwater has a total positive charge of less than 4 mM, the loss of bentonite is calculated with the model developed (Neretnieks et al. 2009). The model can be applied both to the buffer and to the backfill. However, there are a number of uncertainties associated with this treatment:

- The knowledge concerning colloid sol formation and colloid stability is good concerning the effects of mono- and divalent ions. However, modelling of the correlation effects caused by divalent ions is demanding. Since the model basically is based on monovalent ions the calculated loss should be pessimistic.
- The model does not consider face to edge interactions between bentonite platelets. Not considering these interactions probably leads to an overestimation of the loss.
- Filtering effects by accessory minerals could potentially limit or even eliminate the release of colloids from the buffer. However, this is disregarded in the current treatment of the process, since there is a lack of evidence that efficient filters actually form.
- In the model, the expansion has been taken to be horizontal, thus neglecting gravity. Scoping calculations (Neretnieks et al. 2009) suggest that gravity will give small effects as, in the model, the smectite sheets have separated into essentially individual colloid particles. For gravity to have an effect the particles must be considerably larger.
- The concentration limit for cation charge is only based on experimental observations.

Most of the uncertainties are treated with pessimistic assumptions, leading to the conclusion that advective transport conditions in the buffer do not need to be considered in any of the deposition holes during the initial temperate period.

4.3 United Kingdom

RWM is currently in the generic stage of a geological disposal facility (GDF) siting process, therefore detailed studies (colloid-rock interactions) are considered more appropriate at a concept and site(s)-specific level. In the absence of any site(s) for consideration as a potential for a GDF for UK higher activity wastes, the studies undertaken by RWM are generic and consider a range of UK-relevant geologies and UK-relevant disposal concepts.

The assumption of radionuclide sorption reversibility is an important issue. In some situations, to assume reversibility of sorption (onto the rock or near-field materials) is pessimistic because the radionuclide concentration dissolved in the groundwater and the amount of radionuclide that may be sorbed onto colloids may be overestimated. On the other hand, irreversibility of radionuclide sorption onto colloids could increase radionuclide mass transport. The understanding of the reversibility of sorption of radionuclides to colloid surfaces needs to be improved to allow better representation in the safety case (i.e. rates of adsorption/desorption processes). This is likely to be conducted once a UK site(s) has been identified.

If sorption to colloids is found to show significant irreversibility and colloid particles are found to persist on a site-specific basis, 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 (Swanton et al. 2009). 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. A key conclusion of Swanton et al. (2009) stated that 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 radionuclides irreversibly bound to near-field colloids. This is an area which will need to be investigated and understood during the site-specific stage.

5 Synthesis of issues

As explained in Section 1, colloids may be mobile in groundwater and are thus potentially significant because they have been shown to be able to sorb radionuclides and increase their effective concentration in groundwater above that which would be transported in dissolved form. Colloid facilitated transport of radionuclides may be significant if several criteria are met. The decision tree shown in Figure 5-2 can help to form a basis of assessing the potential importance of colloids. By answering a series of questions concerning possible colloid behaviour and considering the underpinning evidence, this can provide a framework for how colloids are treated in a particular safety assessment.

In Sections 5.1, 5.2, 5.3 and 5.4 of this report, progress that has been made as a result of the work undertaken within the BELBaR project against the issues is reported, along with a discussion of the extent of the potential to review the treatment of colloids in performance assessment.

5.1 Erosion

The mechanisms of bentonite erosion from compacted bentonite were investigated in WP2 to better understand the effect of erosion on the integrity of the compacted bentonite buffer in the KBS3 concept over the long-term; and the stability of colloids generated in terms of the significance of the role that they could play in facilitating radionuclide transport in groundwater. The following sections provide a summary of the issues identified at the outset of the BELBaR project, a summary of the conclusion of the experimental programme (as reported in the WP 2 Final Report (Schatz et al. 2015)) and a discussion of the potential implication of the findings for the safety assessment.

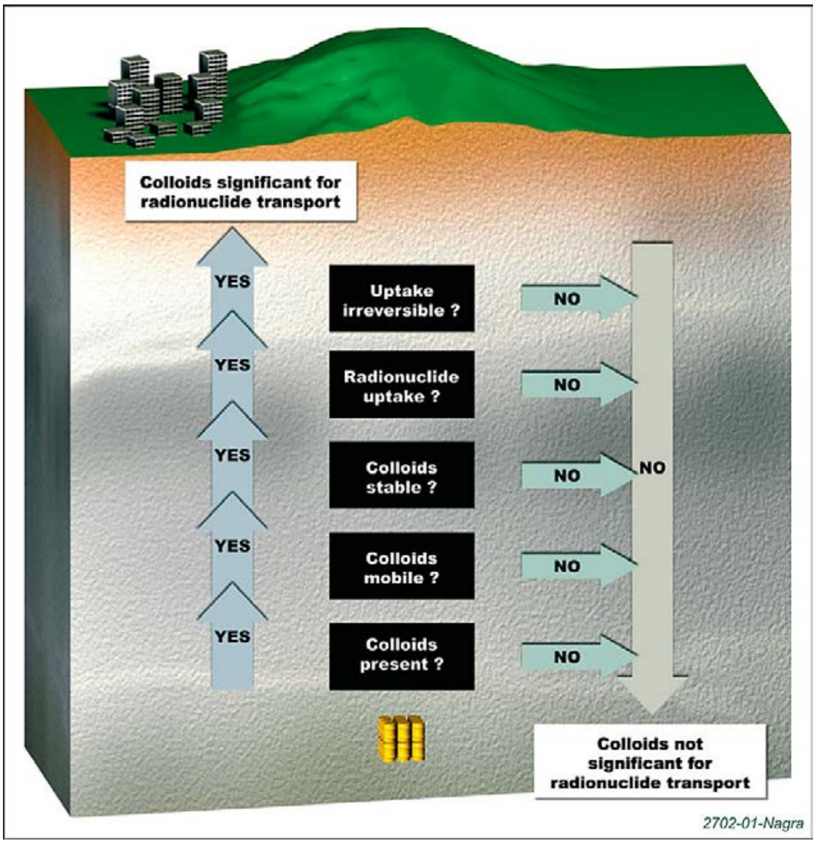

Figure 5-2. *Basis for assessing the potential importance of colloids in performance assessment.*

5.1.1 Mechanisms of erosion of clay particles from bentonite

Safety case position at start of BELBaR
Erosion will cause a loss of bentonite buffer performance under some conditions.
This may lead to corrosion failures of the canisters.
Corrosion failure leads to the largest impact on risk, a less pessimistic approach may have significant impacts on the calculated risk.

The following key points reflect a summary of WP2 conclusions:

- In general, in experiments, erosion/colloid generation is rapid initially, but decreases with time and in some cases stops altogether.
- In static experiments – equilibrium is reached – the maximum quantity of colloids generated depends on initial conditions, e.g, the material used, but erosion is not continuous.
- Chemical forces driving dispersion processes are considered to be more important than mechanical forces even in the dynamic system.
- There is a potential connection between flow rate and erosion when ionic strength of groundwater is below the critical coagulation concentration (CCC)

With respect to the safety assessment, these results suggest that the assumptions documented by the WMOs related to the mass loss rate's dependency on groundwater flow velocity could potentially be reviewed under no highly "erosive" conditions. The activities in WP2 have demonstrated that the mechanism for bentonite erosion overall is driven more significantly by chemical forces rather than mechanical forces. This may be particularly relevant when considering the differences reported in the experimentally derived, or numerical modelling derived values for n within the expression: mass loss scales with flow velocity u as $k \times u^n$ and that potentially the coupling between mass loss and groundwater velocity alone is over estimated in the numerical models.

5.1.2 Characteristics of bentonite clay

Safety case position at start of BELBaR
Some aspects concerning divalent cations have not been studied that systematically.
Should it be possible to verify the existence and quantitative effect of divalent cations on the stability of colloids, the importance of this outstanding uncertainty would be reduced.

The following key points reflect a summary of WP2 conclusions:

- With higher compaction of bentonite clay, the quantity of particles produced is observed to be higher.
- Higher erosion is observed in Na-exchanged bentonites. In Na/Ca-bentonite (e.g. FEBEX), a quantity of Na at 20–25 % is enough to favour colloid generation, comparable to that observed in a Na-homoionised clay.
- Low (and sometimes no) erosion observed in Ca-exchanged bentonites – even under low ionic strength conditions.
- Observed maximum eroded mass is thought to be related more to the montmorillonite (swelling clay) content of the clay rather than the presence of exchangeable Na. The importance of this is confirmed through observation that non-swelling minerals such as kaolinite or illite do not generate colloids. The type of clay in the smectite group is also important as saponite and beidellite do not show appreciable erosion. FEBEX clay mixed with illite showed erosion proportional to the amount of montmorillonite, but the addition of kaolinite totally inhibits erosion.

These results provide an interesting insight into the effects of not only the presence of mono or divalent ions within the bentonite exchange complex, but also the effects of the presence of montmorillonite in terms of increasing the observed mass loss and non-swelling clay minerals such as illite or kaolinite in playing a role in decreasing or inhibiting mass loss.

This is an important observation in terms of the assumptions used by the WMOs regarding the composition of the clay where currently all exchanger site are assumed to be occupied by Na. Therefore the effects of the presence of a divalent ion such as Ca in the exchanger sites or the type of smectite in the clay is not considered. This leads to an overly pessimistic mass loss calculated in the numerical models. However, the modelling capability does not yet exist to take into account the complexity of modelling the correlation effects caused by divalent ions and thus within these limitations this conservative treatment is considered to be appropriate. In a natural system it may also be difficult to exclude that the sodium content in the clay will be less than 20–25 %.

5.1.3 Groundwater chemistry

Safety case position at start of BELBaR
The key factor for colloid stability is the ionic strength and the content of divalent cations.
pH should have an effect, but the pH-range considered in the safety case is rather limited.

The following key points reflect a summary of WP2 conclusions:

- Ionic strength of groundwater is an important factor with respect to erosion.
- In general it has been observed that increasing ionic strength, decreases colloid generation.
- The presence of divalent cations in solution (Ca^{2+}) are more effective than monovalent cations (Na^{+}) as coagulants.
- At a sufficiently high fixed ionic strength in a dynamic (flowing) system, the presence of Ca^{2+} in solution inhibits erosion and the formation of colloids.

As observed and previously recorded, ionic strength is not the only parameter that affects the formation and stability of colloids. As indicated, the presence of different cations in solution can effect coagulation, with divalent cations being more effective than monovalent ions as coagulants. This emphasises the need for appropriate site characterisation during the siting and implementation of a GDF to understand the geochemical bounds of the system to enable and understanding the impacts it will have on evolution. Given that deionised water may not be representative of a real dilute groundwater, it may be considered that erosion for a water with no charge is an overly conservative scenario. However it is considered that this assumption remains appropriate within the overall system uncertainties, particularly with regard to the need to address the potential for a change in groundwater composition, for example due to glacial meltwater.

Another assumption to consider is that mass loss ceases when groundwater salinity exceeds a stability limit of 4–8 mM NaCl for Na-bentonite (Nykyri et al. 2008). Clearly this assumption is linked to the assumed composition of bentonite as explained in Section 5.1.2 where the exchanger sites in the clay are assumed to only be occupied by Na^{+}. Should the assumed composition of the clay be reviewed (and consideration given to the presence of Ca^{2+} or the smectite content) then consideration should also be given to addressing the conservatism that would be inherent in the assumed bentonite stability limit. Within the bounds of the current knowledge, however, it considered that this assumption remains appropriate.

5.1.4 Clay-groundwater interactions

Safety case position at start of BELBaR
Changes in bentonite porewater solute concentrations can be modelled.
The related rates assumed to be limited by the availability of different porewater solutes.
Mass loss rate assumed to have hydrodynamic contribution.
The buffer and the groundwater never reach a true equilibrium.

The following key points reflect a summary of WP2 conclusions:

- Groundwater evolution in the long term will affect the chemistry of the clay/groundwater system.
- It is unlikely that mechanical shear is the key mechanism to perturb a gel phase.
- The hysteresis effect could enable clay to be more stable to erosion.
- Calcium incorporation in an open/dynamic system could reduce/eliminate the production of colloids.

Linked to the experimental findings discussed in Section 5.1.3, it has been observed that in an open system, with a constant supply of Ca^{2+} and when the concentration of Na+ in the clay complex at the gel front is decreased, then colloid generation ceases. This may be an important factor in the long term, since in a system with continuous calcium supply (which would depend on the specific groundwater chemistry at a specific site) calcium saturation of the bentonite surface could result in cessation of colloid generation. Further, an observation has been made that a hysteresis effect may be relevant, that is, the history of the clay and the conditions it has experienced may affect its erosion behaviour. If the clay had previously been subject to high salinity conditions, but these were replaced with more dilute conditions, then the clay was observed to be more resistant to erosion. These types of process are not currently considered in the safety assessment. To consider the dynamic exchange of Na^{+} and Ca^{2+}, a very detailed understanding of the future evolution of groundwater chemistry would be needed. The positive effect of hysteresis is a new finding that has been realised during the BELBaR project; it could potentially have a large impact on the view of gel stability. However, the experimental evidence and the conceptual understanding is still limited. Thus the current conservative treatments are considered to be appropriate.

5.1.5 Groundwater velocity

Safety case position at start of BELBaR
Groundwater velocity has been considered as a variable.
The loss of bentonite will be affected by the groundwater velocity and it is important to verify this dependence for erosion rates.

The following key points reflect a summary of WP2 conclusions:

- In tests where erosion was observed, erosion is well correlated to groundwater velocity. However, the experimental work does not give a consistent view on how the velocity affects the erosion. There are a number of studies that indicate that the velocity dependence is weaker than what has been assumed in assessment models prior to BELBaR.
- Tests conducted in less dilute conditions saw less mass loss, therefore potentially the use of maximum erosion rates to estimate mass loss could lead to unnecessarily conservative erosion predictions.
- System chemistry was observed to be more relevant than flow velocity in terms of driving erosion processes.

The conclusion and recommendations noted here are strongly linked to those reported previously in Sections 5.1.3 and 5.1.4. It is important to note that when conditions are favourable such that erosion does occur, then groundwater velocity will mobilise the eroded particles, therefore water chemistry is an important factor even under dynamic conditions.

There is a time dependence aspect observed in the experimental programme that indicates that erosion rates are reduced at longer timescales, even when experimental groundwater velocity is increased. This is not currently taken into account in safety assessments.

As previously reported, the system chemistry is thought to be more relevant than groundwater velocity and even in a dynamic system, there is a maximum threshold of colloids generated given a specific set of initial conditions. The duration of the experimental programme (more than 3 years in some cases) provides additional confidence in the observed behaviour than was available previously.

This, in support of the previously reported conclusions reported in Section 5.1.3 would suggest that the current treatment and assumptions related to the correlation between erosion and groundwater velocity could be reviewed with respect to the driving mechanism controlling bentonite erosion.

5.1.6 Clay extrusion paths

Safety case position at start of BELBaR
Fractures have been assumed to be planar with a constant aperture.
Extrusion of clay into a fracture is an integral part of the current model and will have a strong impact on the mass loss.
Piping may occur before full saturation of the buffer under certain circumstances.

The following key points reflect a summary of WP2 conclusions:

- Horizontal and sloped fractures display a different mechanism of mass loss. In horizontal fractures the clay is lost when colloids (or agglomerates) are transported away with the flowing groundwater. In vertical fractures the clay is lost by sedimentation and gravity is the driving force.
- Where all other test conditions are identical, increased slope angle leads to increased mass loss. However, based on a limited number of tests, the effect of slope is observed to be more significant at lower angles (0°–25°) compared to 45°–90°.
- Irrespective of slope, at a cation charge greater than or equal to 8.6 mEq/L the rate of mass loss is effectively zero. This seems to indicate that the strength of the gel is the key factor, which also confirms that the chemistry is the key factor.
- Extrusion of clay into the fracture also needs to be considered as a separate mechanism for mass loss.

The size of the extrusion path is observed to be of primary importance in terms of the quantity of colloids generated. A smaller fracture aperture was observed to generate a significantly lower amount of colloids. This is consistent with a surface-area controlling effect on mass loss.

With respect to the angle of the fracture aperture, an interesting observation has been made that the mass loss mechanisms between a horizontal and sloped fracture are different. The first is controlled by dispersive release, whilst the latter occurs through a process of structural collapse of the extruded mass and sedimentation. The acuteness of the fracture angle is also important since it was observed that as fracture angle increases, the mass loss is greater, although the effect is observed to a greater extent between 0° and 45° compared to 45° and 90°.

It is noted that the current performance assessment assumptions assume a horizontal fracture. The results observed suggest that this treatment may not necessarily be conservative. It is strongly suggested that this assumption is reviewed and potentially further work is required to account for the observed effects of slope angle/gravity.

5.2 Colloid, radionuclide and host rock interaction

The following sections provide a summary of the issues identified at the outset of the BELBaR project, a summary of the conclusion of the experimental programme (as reported in the WP3 Final Report (Schäfer et al. 2016)) and a discussion of the potential implication of the findings for the safety assessment.

5.2.1 Colloid mobility controlling processes

Safety case position at start of BELBaR
Clay colloids have not been considered radionuclide carriers due to the assumed low contribution.
Rather than attempting to develop detailed process models for colloid-facilitated transport, potential mitigating processes are ignored so as to place an upper bound on the possible effect.

The following key points reflect a summary of WP3 conclusions:

- Colloid mobility is affected by:
  - fracture geometry (aperture size distribution and fracture surface roughness),
  - chemical heterogeneity induced by the different mineral phases and
  - chemistry of the matrix porewater (even under the electrostatically unfavourable conditions of colloid attachment in glacial melt water, colloid retention has been observed).

Whether colloid transport of radionuclides should be included in the radionuclide transport calculations can be determined by a scoping calculation using assumed transport lengths, flow velocities and desorption rates for individual radionuclides.

5.2.2 Retention processes

Safety case position at start of BELBaR
Retardation of colloid transport in the far field, will delay the arrival of radionuclides in the biosphere.
The extent of this is not currently taken into account.

The following key points reflect a summary of WP3 conclusions:

- It is confirmed that there is a rather strong retention of colloids in the rock.
- Colloid retention has been observed even at conditions where high mobility was expected, i.e. under unfavourable electrostatic conditions.
- The mechanisms that contribute to colloid retention are not yet fully understood. The retention is dependent on the mineral at the fracture surface. The retention in natural rock fractures is stronger than in artificial acrylic fractures used in the erosion experiments of WP2. However, there is also a relatively strong dependence of fracture orientation (horizontal vs vertical), which may complicate a numerical description of the process.
- There are experiments where no retention is observed, but this is most likely caused by too high loading of colloids or high velocities of the experimental set-up.

The conclusion is that there is a significant retardation of clay colloids in a fracture in the rock. However, the uptake is not complete, which means that colloid transport needs to be considered, if colloids are present. It is clear from BELBaR that colloid retardation should be included in safety assessment calculations. However, the effect may be limited under most conditions and the process could therefore be optimistically neglected.

5.2.3 Radionuclide sorption

Safety case position at start of BELBaR
To assess the possible role of rapid reversible radionuclide sorption/desorption onto colloids in facilitating transport, the following assumptions have been adopted: 1. equilibrium sorption of radionuclides onto mobile and immobile colloids, 2. equilibrium sorption of colloids onto fracture surfaces; and 3. colloid-free matrix pore space (basically a conservative assumption, but still rather realistic for the small pore sizes of granitic rock). Reversible, linear sorption of radionuclides onto colloids has been assumed.

The following key points reflect a summary of WP3 conclusions:

- The understanding of desorption phenomena has been vastly improved.
- Sorption of Cs onto montmorillonite is fully reversible, but not onto illite.
- Desorption of trivalent (Eu(III)) is substantially faster from bentonite colloids than from bulk material.
- Pentavalent nuclides show fast desorption.
- The findings for tetravalent nuclides are less conclusive. It may not be possible to assume full desorption of tetravalent nuclides.
- The assumption of linear sorption is always valid for the concertation range that can be expected for radionuclides.

It is clear that the assumption of linear sorption is valid. Sorption reversibility is nuclide specific and should possibly be treated on a case by case basis. However, for most radionuclides sorption reversibility can be assumed over repository time scales. The exception may be tetravalent elements where some caution should be taken.

5.3 Colloid stability

The following sections provide a summary of the issues identified at the outset of the BELBaR project, a summary of the conclusion of the experimental programme (as reported in the WP 4 Final Report (Missana et al. 2016)) and a discussion of the potential implication of the findings for the safety assessment.

5.3.1 Colloid stability controlling processes

Safety case position at start of BELBaR
Stability of compacted bentonite in dilute porewater conditions has been evaluated by laboratory measurements. The controlling process is hydration of exchangeable cations limited by the availability of cation free water. Currently the uncertainties in the effect of geochemical conditions are greater than in uncertainties in the stability limit. Colloid stability studies have found that model colloids that possess a significant net negative charge at neutral pH, i.e. silica and illite clay, show the greatest stability under neutral pH conditions.

The following key points reflect a summary of WP4 conclusions:

- Colloid stability is influenced by the differing mineralogy of different bentonites.
- There is an apparent hysteresis effect where aged gels are observed to be stronger.

Both the erodibility of the clay and colloid transport in the environment are related to groundwater chemistry, the intrinsic properties of the colloids and their stability. Understanding the chemical conditions that favour or do not favour stable colloidal systems helps our understanding of the likely conditions which would favour clay erosion and colloid transport. Parameters that promote the stability of colloids are also favourable in terms of clay erosion and therefore understanding stability is very important in this context.

The composition of bentonite was shown to be important to clay erodibility in WP2 (Section 5.1.2) and a theoretical basis for understanding for the effect of divalent Ca^{2+} on clay gel stability in WP4. A self-consistent, weighted correlation approximation to density functional theory was developed to describe the structural and thermodynamic properties of counter ion-only electrical double layers. The predictions developed agreed well with the Monte Carlo simulations and show that Ca- bentonite would behave essentially as Na- bentonite where the fraction of surface charge neutralised by Na+ is more than 30 %. This has been observed in the region 20–30 % experimentally.

Linked to the recommendations given in Section 5.1.2, the effects of the presence of a divalent ion such as Ca^{2+} in the exchanger sites is not currently considered in performance assessment. This leads to an overly pessimistic mass loss calculated in the numerical models. However, the modelling capability does not yet exist to take into account the complexity of modelling the correlation effects caused by divalent ions and thus within these limitations this conservative treatment is considered to be appropriate, particularly since it remains true that the uncertainties in geochemical conditions are greater than the uncertainties in colloid stability limits.

5.3.2 Influence of other factors on colloid stability

Safety case position at start of BELBaR
Accessory minerals seem to enrich near the bentonite-groundwater interface.
Filtration has been discussed as a possible means to reduce erosion.
Colloid size, solution ionic strength and water flow rate are factors which strongly influence colloid migration.
Association of inorganic particles with natural organic compounds is an important mechanism for colloid stabilisation.
This mechanism could potentially operate to stabilise and enhance colloid populations in the near-field porewater; this remains an area of uncertainty.

The following key points reflect a summary of WP4 conclusions:

- Na and K (M^{+}) and Mg and Ca (M^{2+}) act in a similar way during coagulation processes.
- Interaction of smectite with a mineral such as kaolinite or Al_2O_3 produces aggregation of particles.
- Organic matter is able to stabilise colloids in NaCl electrolyte.
- In $MgCl_2$ and $CaCl_2$, clay colloids undergo fast coagulation independently of the presence of organic matter.

Sodium and potassium, and magnesium and calcium act in similar ways during the coagulation process; and in real systems (e.g. natural groundwater) their effect can be simplified to the effect of M^{1+} (Na, K) or M^{2+} (Ca, Mg) cations, where M^{2+} are more effective in coagulation. The interaction of smectite with minerals such as kaolinite or Al_2O_3 produces the aggregation of particles that, alone under the same chemical conditions, would be stable; this means that the presence of certain minerals not only inhibits the clay colloid generation by 'dilution', but also may affect the properties of the smectite itself making the system unstable. During the investigations the effect of hysteresis was observed with attractive forces in the gels increasing with aging. One week of resting produced significantly stronger gels than those tested after 24 hours.

Organic matter (such as humic or fulvic acids) was demonstrated to be able to stabilise clay colloids in NaCl electrolyte. This means that in the presence of organic matter more concentrated NaCl electrolyte is needed to coagulate clay dispersion (the CCC is higher).

In all the other electrolytes investigated ($CaCl_2$, $MgCl_2$) and at higher ionic strength, the clay colloids undergo fast coagulation, independently of the presence of organic matter. This is true in various aqueous media containing different inorganic cations, showing that the ionic strength remains the key parameter. In addition, calcium ions alone are able to initiate clay colloid agglomeration even at low concentrations. The presence of this inorganic cation, even at only low concentration in natural media, is thus recommended to be considered in performance assessments, as has been highlighted previously.

5.4 Conceptual and mathematical models

The following sections provide a summary of the issues identified at the outset of the BELBaR project, a summary of the conclusion of the experimental programme (as reported in the WP 5 Final Report (Neretnieks et al. 2016) and a discussion of the potential implication of the findings for the safety assessment.

5.4.1 Current model(s): Erosion of the bentonite buffer

Safety case position at start of BELBaR
The factors considered are; 1. groundwater velocity, 2. fracture aperture, 3. transport resistance of bentonite gel in terms of diffusivity, 4. gel cohesivity in terms of viscosity. Small-scale tests suggests groundwater ionic strength and the presence of divalent cations are the dominant factors. Pessimistic assumptions neglecting safety promoting aspects have been used.

The following key points reflect a summary of WP4 conclusions:

- The results from the models developed within BELBaR can match the experimental results from small scale laboratory tests.
- The formation of bentonite flocs in the gel/sol interface needs to be considered in a quantitative model.
- The effect of gravity and the sedimentation of bentonite in fractures need to be considered in a quantitative model.
- A coupled expansion/erosion model that can consider all relevant processes can be challenging to implement numerically, thus simplifications in equations as well as in assumptions may be needed.
- The models predict a large penetration distance of clay gel into fractures.
- The models can be used as an upper bound in safety assessments.

At KTH model development yielded a “two-region model” in which a rim area is discretised in far higher resolution than the rest of the domain; the bulk of the domain is assessed by solving a set of partial differential equations whilst the behaviour at the rim is evaluated by an ordinary differential equation. When assuming a specific volume fraction (ϕ_R) at the rim that the triggers the release of smectite particles (flocs) by diffusion (from the gel to the flowing water), with $\phi_R = 0.015$ as an input in the "two-region model", the match with the small-scale experimental results is very good.

The smectite loss from a deposition hole by smectite agglomerates/flocs pulled by gravity is restrained by the rate of agglomerate transport in the fracture. In fractures smaller than 0.1 mm it is found to be less than 10–100 g/a from a deposition hole in a KBS-3 type repository that is intersected by a semi-vertical fracture. This is of the same order of magnitude as the loss by erosion in horizontal fractures.

Finer grids were tested, as well as simplified equations together with simplifications assuming a) steady state, b) solids concentration gradient in the direction of the flow as being much smaller than that in the cross-stream direction to it (i.e. omitted), c) cross-stream velocity being much smaller than that in the stream wise direction (i.e. omitted) and d) diffusive mass loss at the outer rim. The result was an ordinary differential equation instead of a set of partial differential equations. When comparing the results the erosion rate was some 5 % smaller in the simplified methods when compare to the full method.

When estimating the system, scaling with respect to the size of the source, by solving the simplified full resolution model, the mass loss and the penetration depths can be estimated. According to these simulations clay mass would be lost the closer to the source the higher the water velocity. The exponent in the mathematical fits is 0.31 (i.e. $Flux = 0.73 \times (v \times R)^{0.31}$) suggesting relevant dependence of mass loss rate on velocity. At low velocities the penetration of the clay front into the fracture can be substantial. There is not however experimental evidence for or against clay penetrating tens of metres into fractures.

It can be stated that a new bounding estimate is proposed to be used in the safety cases to assess clay mass loss rates; loss of clay at the clay-water interface is limited by migration of newly formed clay agglomerates in fractures. This estimate, based on specific volume fractions, can be obtained with far less effort and uncertainty than the estimates used in the previous safety cases.

5.4.2 Current model(s): Radionuclide transport mediated by bentonite colloids

Safety case position at start of BELBaR
Clay colloids have not been considered radionuclide carriers in Posiva's safety case due to the assumed low contribution. SKB incorporated the effective transport parameters using the MARFA code. At the colloid concentrations likely in the far field, a significant increase in risk could arise if a proportion of the radionuclides associated with colloids are irreversibly sorbed. In that case the risk will depend on the mobility and particle lifetimes.

No further development of quantitative models for radionuclide transport mediated by bentonite colloids has been performed in BELBaR. The conclusions from WP3 are therefore valid for this issue as well. Whether colloid transport of radionuclides should be included in the radionuclide transport calculations can be determined by a scoping calculation using assumed transport lengths, flow velocities and desorption rates for individual radionuclides. It is clear from BELBaR that colloid retardation should be included in safety assessment calculations. However, the effect may be limited under most conditions and the process could therefore be optimistically neglected. It is clear that the assumption of linear sorption is valid. Sorption reversibility is nuclide specific and should possibly be treated on a case by case basis. However, for most radionuclides sorption reversibility can be assumed over repository time scales.

6 Summary of recommendations

The BELBaR project was a collaborative project based on the desire to improve the long-term safety assessments for geological disposal facility concepts for spent fuel/high level waste that combine a clay engineered barrier system (EBS) with a fractured rock.

Colloids may be mobile in groundwater and are thus potentially significant for safety because they have been shown to be able to sorb radionuclides and increase their effective concentration in groundwater above that which would be transported in dissolved form.

The main aim of the BELBaR project was to increase the knowledge and reduce uncertainties with respect to the processes that control clay colloid generation, stability and ability to transport radionuclides; and reduce the uncertainties in the description of the effect of clay colloids in long-term performance assessments.

A reduction of uncertainties in the understanding may lead to:

- Reduction of the assessed overall radiological risk from a repository.
- The possibility to totally neglect the process in assessments under some circumstances.
- Guidance to future site selection and site characterisation programmes.
- Guidance in the selection of engineered barriers for a nuclear waste repository.

This report provides a synthesis of the progress that has been made as a result of the work undertaken within the BELBaR project along with recommendations for the potential to review the treatment of colloids in performance assessment. The following points represent a summary of recommendations[2]:

1. With respect to the safety assessment, the results of BELBaR suggest that assumptions made by WMOs relating to the dependency of mass loss rate on groundwater flow velocity could potentially be reviewed under no highly 'erosive' conditions. It has been shown that bentonite erosion overall is driven more significantly by chemical forces rather than mechanical forces and thus it is recommended that the current treatment could be reviewed with respect to the driving mechanism controlling bentonite erosion.
2. All exchanger sites in the clay are currently assumed to be occupied by Na^+. This assumption leads to high erosion rates and overly pessimistic mass loss calculations since the current modelling capability is not able to take into account the effects of divalent cations such as Ca^{2+}. However, in a natural system, it would be difficult to exclude that the Na content of clay is less than the 20–25 % threshold that favours colloid generation and thus the current treatment is considered to be appropriate within the overall system uncertainties.
3. The presence of different cations in solution can effect coagulation, with divalent cations being more effective than monovalent ions as coagulants. It is currently assumed that mass loss ceases when groundwater salinity exceeds a stability limit of 4–8 mM NaCl for Na-bentonite (Nykyri et al. 2008). Should the assumed composition of the clay be reviewed (Recommendation 2) then consideration should also be given to addressing the conservatism that would be inherent in the assumed bentonite stability limit. However, within the bounds of the current knowledge, it considered that this assumption remains appropriate.
4. In terms of the ionic strength of groundwater assumed, given that deionised water may not be representative of a real dilute groundwater, it may be considered that the maximal zero charge limit is an overly conservative scenario. However it is considered that this assumption remains appropriate within the overall system uncertainties, particularly with regard to the need to address the potential for a change on groundwater composition for example due to glacial meltwater.

[2] Recommendations may be considered most relevant to site-specific assessments.

5. With respect to the angle of the fracture aperture, it is observed that the mass loss mechanisms between a horizontal and sloped fracture are different. Current performance assessment assumptions are based on a horizontal fracture and thus the results observed suggest that this treatment may not necessarily be conservative. It is strongly suggested that this assumption is reviewed and potentially further work is required to account for the observed effects of slope angle/gravity.
6. Significant retardation of clay colloids in a rock fracture has been observed. However, the uptake of colloids is not complete (i.e. some remain in solution), which means that colloid transport needs to be considered, if colloids are present. It is recommended that colloid retardation could be included in safety assessment calculations. However, the effect may be limited under most conditions and the process could therefore be optimistically neglected.
7. It is clear that the current assumption of linear radionuclide sorption is valid. Sorption reversibility is nuclide specific and should possibly be treated on a case by case basis. However, for most radionuclides sorption reversibility can be assumed (the exception is potentially tetravalent elements where caution should be taken) over repository time scales.
8. Organic matter (humic or fulvic acid) was demonstrated to be able to stabilise clay colloids in NaCl electrolyte. In all the other electrolytes investigated ($CaCl_2$, $MgCl_2$) and at higher Ionic strength, the clay colloids undergo fast coagulation, independently of the presence of organic matter. This is true in various aqueous media containing different inorganic cations, showing that the ionic strength remains the key parameter. In addition, Ca^{2+} ions alone are able to initiate clay colloid agglomeration even at low concentrations. The presence of Ca, even at only low concentration in natural media, is thus recommended to be considered in performance assessments (as per Recommendations 2 and 3).
9. Regarding validation and advancing the models, sufficient confidence was obtained to predict clay mass loss rate on laboratory scales using numerical simulations, whereas mass loss rate predictions on repository relevant scales remain to be assessed using analytically derived expressions for bounding estimates. According to the bounding estimates referred to, the agglomerate/floc migration rate in fracture is the mass loss rate determining feature.
10. The reasoning of dominant processes was succeeded considering agglomerate migration but was based only on expert judgement for clay swelling and gravity. Moreover, data needs specifications to assess the relative importance of clay swelling and gravity were raised but only when it was too late to commit experiments within BELBaR.
11. It can be stated that a new bounding estimate is proposed to be used in the safety cases to assess clay mass loss rates; loss of clay at the clay-water interface is limited by migration of newly formed clay agglomerates in fractures. This estimate can be obtained with far less effort and uncertainty than used in the previous safety cases.

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