A Review of Cellulose Degradation and the Fate of Degradation Products Under Repository Conditions
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A Review of Cellulose Degradation and the Fate of Degradation Products Under Repository Conditions

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Abstract

The disposal of long-lived intermediate- and some low-level wastes (ILW/LLW) in vaults backfilled with cementitious material is one of a number of generic disposal concepts under consideration in the UK. The employment of a cementitious backfill results in the generation and persistence of a high pH (pH 12.5 to 10.5) environment within the disposal system. These conditions are favourable in terms of reducing the mobility of some radionuclides, however they also promote the chemical degradation of cellulosic materials present in some wastes. This alkaline chemical degradation of cellulose results in the generation of a range of soluble products some of which are able to complex radionuclides and potentially enhance their mobility (e.g. iso-saccharinic acid). This report reviews the current understanding regarding alkaline cellulose degradation and the associated impacts of radiolytic and microbial processes. Conceptual and mathematical models developed to describe alkaline cellulose degradation are also outlined and discussed. The nature and extent of alkaline cellulose degradation products are discussed together with their stability towards microbial and chemical degradation under repository and geosphere conditions. Finally the report discusses the treatment of alkaline cellulose degradation and the resulting cellulose degradation products in performance assessments.

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Executive Summary

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. It is currently intended that all UK higher-activity wastes will be disposed of in a single facility, providing that this facility can be developed to provide suitable, safe containment for the waste inventory. At present, a number of generic disposal concepts are under consideration by the NDA. These include one illustrative concept for the disposal of long-lived intermediate- and some low-level wastes (ILW/LLW) in a disposal area backfilled with cementitious material.

The cement-based disposal concept for ILW/LLW is a multi-barrier disposal concept that includes the chemical conditioning of waste and vault environments through waste grouting and vault backfilling with cementitious materials. This conditioning will ensure that alkaline anaerobic conditions dominate the repository environment for long periods post closure. This chemical environment will have a significant impact on organic materials such as paper, wood and cotton present within the waste since cellulosic materials are susceptible to alkaline degradation. This is of interest because alkaline cellulose degradation produces soluble organic compounds able to form complexes with disposed radioelements, enhancing their migration and potentially increasing the associated radiological risks. Alkaline degradation of cellulose generates a range of organic compounds with α and β isosaccharinic acid (ISA) being the most abundant. Although these isomers of ISA are produced alongside a wide range of short chain organic acids, it is ISA which has received most attention due to its complexing ability.

Current models of alkaline cellulose degradation involve three phases which control the overall rate and extent of reaction. The first phase is an initial rapid degradation dominated by the peeling of end groups followed by a second slower phase where the peeling reaction is inhibited by a combination of physical and chemical stopping reactions; further degradation is controlled by the physical access to available end groups and the rate at which new end groups are released by mid-chain scission of amorphous portions of the cellulose. The final phase is dominated by stopping reactions which occur when mid-chain scission runs out of amorphous cellulose and is physically inhibited by crystalline regions of the cellulose fibres. There is disagreement as to whether degradation ceases at this point or continues over the long term via currently undefined reaction pathways which allow peeling reactions and/or mid-chain scission to proceed. In particular the impact of the degree of crystallinity on the long-term rates of reaction and the evolution of crystalline regions into amorphous regions are in need of further clarification. However, given that there is clear evidence that radiolytic degradation of cellulose enhances alkaline cellulose degradation through the generation of end groups amenable to peeling reactions, any further research in this area should incorporate the impact of relevant radiation fields. Clarification of the mechanistic basis of the long term alkaline degradation of cellulose at temperatures and radiation fields relevant to radioactive waste disposal sites is a clear area for further research. An improved understanding of these processes will reduce uncertainties associated with the rates of ISA generation and ultimate ISA concentrations employed in PA calculations.

Currently there appear to be little or no experimental data on radiolytic impacts on cellulose degradation products and ISA in particular. Data on the chemical stability of ISA indicate that it is stable in the absence of oxygen or other oxidising agents suggesting that potentially oxidising conditions generated by radiolysis could play a role in the removal of ISA from the near-field of a repository. Confirmation of the impact of radiolysis on near-field complexant concentrations would be beneficial.

Microbial degradation of ISA has been described but only under aerobic and denitrifying conditions. Whilst there is no reason to believe that microbial ISA degradation cannot take place under the anaerobic conditions of a repository there is no direct evidence available at present. The high pH which will dominate the repository environment for many years post closure is likely to confine microbial activity to low pH niches within the near-field environment. In the geosphere, interactions between the plume leaving the near-field and the prevailing geochemistry will attenuate the plume...
pH increasing the likelihood of microbial activity. Microbial degradation of ISA under geosphere
conditions has not been an area of significant research to date.

In view of the impact of ISA (and other cellulose degradation products) on radioelement migration
its production and impacts have been incorporated into radiological performance assessments. The
extent of alkaline cellulose degradation has been incorporated into performance assessments via
log triangular probability density functions (PDFs). Current PDFs, revised in 2006, are based on
data available at that time on the likely extent of alkaline cellulose degradation. Currently there are
insufficient new data to justify modifying the existing PDFs. If data supporting an enhanced rate of
long-term alkaline cellulose degradation emerge then the PDFs would need to be updated
accordingly. In particular data on radiation enhanced alkaline cellulose degradation are likely to
necessitate a revision of the current PDFs. In addition, further data are required concerning the
properties of cellulosic waste materials to inform the elicitation of the proportion of reactive
cellulose.

This report was prepared by Serco Technical and Assurance Services and the University of
Huddersfield under contract to NDA RWMD. The main technical work reported here was carried
out in the period January to May 2008 and the report is based upon information available at that
time. Thus, for example, where the report refers to ‘current knowledge’ this should be read to
mean ‘knowledge existing at the time the work was carried out’. The work forms part of the NDA
RWMD research programme. The information has been verified under arrangements established
by Serco Technical and Assurance Services. These arrangements have been approved by NDA
and are consistent with ISO 9001.

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1 Introduction

As part of its Managing Radioactive Waste Safely (MRWS) programme, UK Government issued a White Paper in June 2008 setting out a framework for implementing geological disposal of the UK's higher activity radioactive waste [1]. It is currently intended that all UK higher-activity wastes will be disposed of in a single facility, providing that this facility can be developed to provide suitable, safe containment for the waste inventory. At present, a number of generic disposal concepts are under consideration by the NDA. These include one illustrative concept for the disposal of long-lived intermediate- and some low-level wastes (ILW/LLW) in a disposal area backfilled with cementitious material [2, 3] (Table 1, Figure 1).

In the cement-based disposal concept for ILW/LLW, 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, and at a time determined by future generations. The backfill provides alkaline conditions 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 anaerobic alkaline conditions will prevail for much of the repository’s lifetime. The operation of the repository will involve a number of phases starting with the packaging of the waste and finishing with the long term monitoring of the closed repository. This repository lifetime includes period of surface and subsurface storage [2, 3](Table 1).

The solubility and sorption of radioelements are key factors that would determine the release of radioelements from the near field of a deep geological repository. One possible influence on radioelement solubility and sorption is the formation of water-soluble complexants by the degradation of the solid organic materials that will be present in ILW and LLW [4]. Volumetrically, the most important potential sources of organic complexants will be cellulosic materials such as paper, wood and cloth present in the wastes. Cellulosic materials have been shown to degrade under the alkaline conditions relevant to a cementitious radioactive waste repository, and the resulting cellulose degradation products (CDPs) are able to complex some radioelements, potentially causing solubility enhancement under near-field conditions and sorption reduction under both near-field and geosphere conditions [4, 5]. The most important CDP is isosaccharinic acid (ISA).

A considerable amount of work has been carried out to investigate the rate of the alkaline degradation of cellulose in the context of a cementitious repository both in the UK (e.g. [6]) and abroad (e.g. [7, 8]). The effects of α-radiolytic degradation of cellulose on plutonium leaching and solubility (relevant to plutonium contaminated material (PCM wastes)) [9] and the effects of γ-irradiation [10] have also been investigated. These are the only examples of experimental work where alkaline and radiolytic cellulose degradation have been combined. Such work has been used as a basis for eliciting the extent of the degradation of cellulose over the timescales of interest in performance assessments [11]. Further measurements on the long-term degradation of cellulose under alkaline conditions have recently been described that extend the period of experimental observation to approximately 12 years [12]. The identity and further chemical degradation of the products (e.g. isosaccharinic acid (ISA)) under alkaline conditions has also been investigated (see for example references [13-16]). In addition to chemical degradation, cellulose and CDPs can also be degraded through microbial activity [17, 18]. The nature and extent of microbial activity is determined by the prevailing physical and chemical conditions.

This report summarises the current knowledge concerning the rate and extent of cellulose degradation with time under repository conditions, the identification of degradation products and the stability of those species (in particular ISA) under near-field and geosphere conditions. The
current probability density functions (PDFs) for the extent of cellulose degradation with time over the timescales of interest in performance assessment have been reviewed. The potential mobility of CDPs under geosphere conditions have not been addressed in detail to date in radioactive waste management programmes; the current state of knowledge in this area is also included in this review.

The report is structured as follows; Section 2 provides an introduction to cellulose chemistry and the sources of information used for this review. Section 3 outlines the current understanding of cellulose degradation under repository conditions. The stability of CDPs under repository conditions is discussed in Section 4 and their migration and persistence in the geosphere are discussed in Section 5. An overview of the current treatment of cellulose degradation in performance assessment (PA) calculations is given in Section 6. The current state of knowledge concerned cellulose degradation is summarised and some of the outstanding issues are highlighted in Section 7.

This report was prepared by Serco Technical and Assurance Services and the University of Huddersfield under contract to NDA RWMD. The main technical work reported here was carried out in the period January to May 2008 and the report is based upon information available at that time. Thus, for example, where the report refers to ‘current knowledge’ this should be read to mean ‘knowledge existing at the time the work was carried out’. The work forms part of the NDA RWMD research programme. The information has been verified under arrangements established by Serco Technical and Assurance Services. These arrangements have been approved by NDA and are consistent with ISO 9001.

The views expressed and conclusions reached are those of Serco Technical and Assurance Services and the University of Huddersfield and do not necessarily represent those of NDA.

2 Introduction to Cellulose Chemistry

The cellulosic materials present in LLW and ILW (cotton, paper and wood) are composed of a range of polymeric material which reflects their origins and the degree of processing. Cotton is composed primarily of cellulose, whereas wood and paper contain a range of polymers. Wood contains significant amounts of both cellulose and hemicelluloses whereas the hemicellulose content of paper is much lower (<10%) and depends on the raw material used (hard or soft wood) [19]. In addition to cellulose (50%) and hemicellulose (20-35%), wood also contains lignin (15-30%) [20]. Lignin is an aromatic polymer, which forms cross links with the polysaccharide components of wood providing mechanical strength and resistance to microbial degradation [21]. The lignin present in wood is removed during the manufacture of paper leaving cellulose and reduced amounts of hemicellulose. The Kraft Pulping process used to manufacture paper involves heat treating the raw polysaccharides with strong alkali which allows the extraction of the cellulose fibres from the highly branched lignocelluloses. This process influences both the degree of polymerisation and the crystallinity of the cellulose present. Cellulose and hemicellulose have very different physical and chemical characteristics which have direct relevance to their degradation in repositories e.g. celluloses are insoluble in alkali and hemicelluloses are soluble. Studies on the rate of alkaline degradation of these substrates under repository conditions indicate that celluloses degrade much more slowly than hemicelluloses [8].

2.1 Structure of Cellulosic Material

Cellulose is composed of a chain of repeating cellobiose units (Figure 2) which are disaccharides formed from linking (1,4)-β-D-glucose units together. Each glucose unit is rotated through approximately 180° compared to its neighbours [22]. The twisted backbone and the adoption of the chair (C1) conformation (Figure 2) enables the formation of an intramolecular hydrogen bond network between the 3-OH and the preceding ring O5 (Figure 3 Top). Hemicelluloses on the other hand are branched polymers which contain a range of different monosaccharides. Hemicelluloses from different plant species have different compositions but the major constituents are xylans, galactoglucomannans, glucomannans and arabinogalactans.
Cellulose chains are believed to be biosynthesised with chain elongation occurring from the non-reducing end (Figure 3 Bottom) [19]. These chains are generated in bundles that have the same parallel arrangement of (1,4)-\(\beta\)-D-glucose units i.e. the reducing ends are together. As the chains emerge they form microfibrils and sections of the microfibrils crystallise as they are synthesised generating both crystalline and amorphous regions. Chain lengths within microfibrils have been measured with degrees of polymerisations (DPs) as high as 9700 [23]. An important point for studies of the degradation of cellulosics is that individual chains can pass through a number of amorphous and crystalline regions; material in amorphous regions may not be able to participate in reactions if blocked by a preceding crystalline region. Hemicelluloses have considerably smaller DPs when compared to cellulose. A variety of different crystalline forms of cellulose are known [19]. Cellulose I\(a\), I\(b\) are meta-stable and after recrystallisation or treatment with strong base yield cellulose II. In each crystalline state the patterns of hydrogen bonding differ; the orientation of chains differs between phase I, where the chains are parallel, and phase II where the chains are anti-parallel. The different phases will have different chemical and physical properties although it is not known to what extent these differences influence the alkaline degradation rates of cellulosics.

2.2 Degradation of Cellulosic Materials

In the last two decades a substantial volume of work has been undertaken to determine both the mechanism and rates of degradation of cellulosics under cementitious repository conditions. The published research can be divided into three separate fields: the alkaline decomposition of cellulose; the microbial decomposition of cellulose; and radiolytic decomposition. For each area, the expected environment within a cementitious repository after closure provides a set of boundary conditions for experiments and these include (Table 2):

- anaerobic conditions;
- an initial rise in temperature to approximately 60°C followed by a subsequent fall to 25°C;
- saturation with cement pore water having an alkaline pH, originally expected to be 13.5 but falling to 12.5 as the cementitious materials mature and evolve.

Under alkaline conditions, cellulosic materials degrade chemically to form a range of cellulose degradation products (CDPs) [24, 25]. The two major CDPs are \(\alpha\)-isosaccharinic acid (3-deoxy-2-C-(hydroxymethyl)-erythro-pentanoic acid) and \(\beta\)-isosaccharinic acid (3-deoxy-2-C-(hydroxymethyl)-threo-pentonic acid) [24, 25]. These are formed along side a large number of small chain fatty acids each of which is present in small amounts [15, 25]. The pathways, mechanisms and rates of alkaline cellulose degradation have received considerable attention [4, 5, 8, 13-16, 25, 26] primarily with a view to inform radioelement migration calculations associated with repository performance assessments. Three distinct reaction pathways have been identified which contribute to the alkaline degradation of cellulose [25] which are referred to as the ‘peeling’, ‘stopping’ and ‘mid-chain scission’ reactions (Figure 4 and Figure 5). Early studies on the rate of alkaline degradation of these substrates indicate that cellulosics degrade much more slowly under alkaline conditions than hemicelluloses [8].

Anaerobic microbial degradation of cellulosic materials occurs in a wide variety of environments and consequently has been well studied [17, 20, 27-29]. Under anaerobic conditions complete cellulose degradation involves a number of steps and a wide range of microorganisms ultimately resulting in the production of carbon dioxide and methane or other reduced products such as hydrogen sulphide [17, 29] (Figure 6). A significant amount of research on anaerobic cellulose degradation has focussed on landfill sites since domestic waste contains cellulosic materials such as paper and wood [17]. Although the cellulosic composition is similar, the environmental conditions expected within a radioactive waste disposal sites are quite different to those in landfill sites (e.g. higher pH, lower water availability), and consequently direct extrapolation from domestic waste disposal is not possible [17].

When organic polymers are exposed to ionising radiation, a complex series of radiolytic processes occur. In generic terms, energy is absorbed which results in the dissociation of covalent bonds and
the generation of free radicals. The level of structural change or damage in an irradiated polymer is related to the amount of radiation energy absorbed, or dose (SI unit Gray, Gy). As polymers have a wide range of compositions and structures, their radiation resistance varies and is usually described as the dose required to induce a specific level of change in properties, such as structural integrity.

The free radicals generated during radiolysis of a polymer can react to cause chain scission (molecular weight reduction, degradation) or cross-linking where adjacent chains or molecular groups attach to each other to form a network structure. In most polymer systems these two processes are usually in competition with each other and one usually dominates. In addition, the free radicals can react with their local environment, for example, oxygen to form highly reactive peroxy radicals [30] which can cause oxidative chain scission in a polymer that might normally be expected to cross link. The manner in which radiation induced free radicals react in a polymer and the resultant condition of the material depends on several factors which include:

- the chemical structure of the polymer [31];
- the physical structure/morphology (the level of crystallinity can strongly influence radiation stability [32]);
- the environment in which the polymer is irradiated, (the manner in which a polymer degrades under vacuum can differ markedly compared to irradiation in air);
- temperature (synergy can often exist between thermal degradation and radiolysis where the combined effects are usually more damaging that the sum of the damage of the individual components [33]); and
- the irradiation dose rate (dose rate effects can result in polymer appearing to retain its structural integrity when irradiated at high dose rates but losing its integrity when irradiated to the same dose at low dose rates, factors such as diffusion limited oxidation [34] or the concentration of reactive degradation products strongly influence these processes).

Wastes containing cellulose may receive significant radiation doses both during storage and after backfilling and disposal. Cellulosic wastes will be exposed to both gamma and alpha radiation with the gamma dose rate declining rapidly post closure since its emissions are dominated by $^{60}$Co and $^{137}$Cs [4]. Alpha dose, on the other hand, will be dominated by a significant inventory of long-lived radionuclides [4]. This indicates that a proportion of the cellulose inventory will be subject to significant levels of radiation both pre- and post-closure. It is likely that irradiation will increase the susceptibility of cellulose to alkaline degradation by promoting mid-chain scission and reducing the proportion of recalcitrant highly-ordered material [4]. This is supported by the fact that irradiated wood pulp generated greater yields of ISA than un-irradiated pulp treated in the same manner [35] and the degradation of $\approx 4$ wt% of recalcitrant cellulose when exposed to gamma radiation under alkaline conditions at room temperature [10].

### 3 Current Understanding of Degradation of Cellulose under Repository Conditions

#### 3.1 Approaches to the Study of Chemical Cellulose Degradation

Two strategies have been adopted to study the chemical degradation of cellulose and the associated generation of CDP. First, to study the degradation of cellulose over a number of years (up to 12) and secondly to perform experiments at elevated temperatures [8, 9, 12, 16, 26, 36]. These approaches have been used to generate data that is relevant to repository conditions. Experiments have concentrated almost exclusively on measuring the conversion of insoluble cellulose to alkali soluble organic carbon. The change in the total dissolved organic carbon during the course of the degradation studies is taken as a measure of the total ISA and short-chain fatty acid concentrations. Reaction mechanisms have been proposed to account for the various decomposition products. Rate data has been used to develop kinetic models that can be used to
extrapolate data to the extremely long life-times expected for a repository [8, 26, 36]. However, this extrapolation introduces significant uncertainties into the derived cellulose degradation rates.

To simulate the cellulose components of LLW and ILW, a number of different cellulose based materials have been employed including cotton, tissue, paper and wood. However these materials will have very different properties [19] making comparisons difficult. For example, the ratio of amorphous to crystalline regions will not be the same and the length of the polysaccharides chains (i.e. the DP) will differ. A number of studies have employed materials likely to contain both hydrocellulose¹ and hemicelluloses. Whilst studies have attempted to rationalise differences in the results obtained for the four basic subgroups (cotton, paper, tissue and wood [8, 26, 36]) no real attempt has been made to perform systematic variation of material within the groupings and no attempt has been made to correlate degradation rates with degree of crystallinity. Very little work has been directed at understanding how pre-treatment of cellulose sources employed in the paper production process such as Kraft pulping [19] and Mercerisation [19] influences the rates of reaction. The lack of data relating the structure of the raw material to its rate of decomposition, provides a potential weakness of the current kinetic models and their ability to predict ISA concentrations over extended periods. The consequence of this lack of systematic understanding from a PA perspective is that the mechanistic understanding and associated rates of reaction used to inform the elicitation of PDFs may be unrepresentative of cellulosic waste materials in general and lead to bias in the elicited parameters.

3.2 Summary of Mechanisms and Rates of Chemical Degradation of Cellulose

Three distinct reaction pathways have been identified which contribute to the alkaline degradation of cellulose [25]. The different reactions are referred to as the ‘peeling’, ‘stopping’ and ‘mid-chain scission’ reactions (Figure 4 and Figure 5). Peeling occurs at the reducing end group and involves the conversion of the terminal anhydroglucose unit, via a sequence of chemical steps including the elimination of the cellulose chain, to 3-deoxy-2-C-(hydroxymethyl)-erthyro- and -threo-pentonic acids (ISA). The generation of ISA exposes a new terminal glucose unit and the peeling process can be repeated. An unchecked peeling reaction would eventually lead to the complete degradation of cellulose. Studies of the kinetics of the peeling process, performed at room temperature, indicate that complete degradation does not take place [8] due to ‘chemical’ and ‘physical’ stopping reactions. In the ‘chemical’ stopping reaction, the initial steps of the mechanism parallel those of the peeling reaction but rather than eliminating the cellulose chain a hydroxyl group is eliminated with the formation of 4-O-substituted 3-deoxy-D-arabino and ribo-hexonic acid units (Figure 4, bottom left) which are referred to as metasaccharinic acids (MSAs). The formation of MSAs removes the reducing end group and blocks subsequent peeling of the chain.

The vast majority of celluloses are composed of both amorphous and crystalline regions with individual cellulose chains passing through both [37-40]. The rate of degradation of cellulose is slowed or stopped by the inaccessibility of these crystalline regions, a process known as physical stopping, where the peeling reaction cannot proceed for steric reasons [12]. Therefore, in modelling the alkaline degradation kinetics, it is usual to include a second stopping reaction, a ‘physical’ stopping which is defined as a reduction in rate of the peeling reaction as the chain passes from an amorphous region to a crystalline region. The third reaction which contributes to the alkaline degradation of celluloses is mid-chain scission which is the hydroxide catalysed cleavage of glycosidic links at random sites along the chain. This generates new reducing end groups (Figure 5), which can then participate in the peeling reaction. The two processes of mid-chain cleavage and peeling cannot be studied independently.

The absolute rates of the peeling (assigned a rate constant $k_1$), stopping (assigned a rate constant $k_t$ which is a sum of the rate constants for the chemical and physical stopping reactions) and mid-chain scission reactions (assigned a rate constant $k_{hydr}$) control the extent of degradation of a

¹ Hydrocellulose is a term given to partially hydrolysed cellulose which results in a reduction in the DP.
specific cellulose. This will in turn contribute to the levels of ISAs present in the repository. There is disagreement in the scientific literature regarding the rate constants for the ‘physical’ stopping reaction and there is significant uncertainty in the rates for the ‘mid-chain scission’ reaction [26, 36]. To add to the uncertainty, the rates of these reactions will be influenced by the type of cellulose under study. As stated earlier, the celluloses found in both ILW and LLW are from a variety of sources. Wood and paper contains alkali soluble hemicelluloses and these degrade by similar mechanisms to generate ISAs but, being soluble, are not subject to physical stopping reactions.

Alkaline degradation studies under simulated waste and repository conditions [8, 26, 36] have been carried out to determine the extent of degradation, the resulting degradation products and to derive kinetic parameters. Kinetic parameters were derived by treating the stopping reactions as a single pseudo-first order process and the peeling reaction was treated in a similar manner; the production of ISAs was also represented by a first order kinetic expression. The rate of mid-chain scission was estimated by extrapolation of rate data measured at higher temperatures. The extrapolated data suggested that mid-chain scission was not significant at 25°C [8]. These studies clearly demonstrated that the degree of degradation is related to the mole fraction of end groups available which is related to the DP of the cellulose: the smaller the DP the faster the degradation. It should be noted that this most probably reflects that the dominant reaction being studied in these systems is the ‘peeling’ reaction-see discussion below for results obtained at higher temperatures.

At 25°C, for a fixed DP, degradation proceeds quickly at first, with soluble components and exposed reducing ends being consumed by the peeling reaction. The degradation rate then slows greatly as the number of ends is reduced by stopping reactions. Van Loon and Glaus [8] developed a kinetic expression to model the alkaline decomposition of cellulose at room temperature according to this two-phase model:

\[
(cel\ deg) = \frac{k_i}{k_t}(G_r)_0(1-e^{-k_t})
\]

where:

\( (cel\ deg) \) is the mole fraction of cellulose degraded

\( K_t \) is the first order rate constant for the peeling reaction

\( k_t \) is the overall first order rate constant for the stopping reaction

\( (G_r)_0 \) is the mole fraction of reducing end groups

The rate of mid-chain scission \( (k_{hydr}) \) becomes increasingly important when experimental degradation data is extrapolated to cover longer periods e.g. 1000s of years. The first models ignored the rates of mid-chain scission \( (k_{hydr} = 8.6 \times 10^{-10} \text{ h}^{-1} - 8.6 \times 10^{-12} \text{ h}^{-1}) [8] \) because data extrapolated from rates measured at high temperatures implied only a small amount of cellulose would degrade in the medium term (less than 10% within 1000 years). Mid-chain scission was predicted to only impact the degree of degradation over extended periods e.g. millions of years. In the initial model proposed by Van Loon and Glaus [8] 10^5 years have elapsed before >50% cellulose degradation is observed.

A later study by Pavasars et al. [36], modelling of experiments performed between 3 and 7 years, used non linear analysis to determine kinetic parameters for each of the different reactions. The major difference was that they predicted a substantially higher value for \( k_{hydr} \) \( (2-3 \times 10^{-6} \text{ h}^{-1} \) dependent on cellulose loadings). These authors introduced an extended kinetic scheme:

\[
(cel\ deg) = 1 - (1 - \left(\frac{k_h}{k_t}(G_r)_0(1-e^{-k_t})\right)e^{-k_{hydr}})
\]

When these higher values for \( k_{hydr} \) are used to predict the degree of cellulose degradation for a period of 1000 years there is now almost complete conversion of cellulose to ISA.
Differences between the two studies have been discussed by Glaus and Van Loon [26] who identified weaknesses in their own earlier study. Further experiments were undertaken monitoring the alkaline catalysed degradation of cellulose at elevated temperatures. The additional study generated a number of key findings: the initial rates of cellulose degradation were high but these soon reduced; the degradation appeared to stop after approximately one year and the rate of degradation at elevated temperatures is similar for celluloses of different DPs. The high initial rates are compatible with a high rate constant for $k_{\text{hydr}}$ (equivalent to the number estimated by Pavasars et al. [36]) but this does not explain why degradation slows and appears to halt after a year. The authors proposed an expansion of the model system to include a stopping of the hydrolysis reaction (Figure 7). A three-phase reaction sequence was proposed:

i) an initial rapid peeling off of monomeric units of cellulose;  
ii) this is followed by a phase of slower mid-chain fragmentation catalysed by base which generates new end groups that can participate in the peeling reaction;  
iii) finally a complete stopping of the degradation i.e. of both the peeling and the mid-chain scission. The rate of mid-chain scission reduces to zero as the amount of accessible amorphous material decreases.

The separation of the degradation into phases allows the dependence of rates on DP to be better understood. In the initial phase, peeling will be very dependent on DP; whereas in the second phase, if chain scission is rate-limiting, then DP will not influence the degradation rate. In this three-phase model, the rate of mid-chain scission reduces to zero as the amount of accessible amorphous material decreases. For mid-chain scission to continue, the transformation of crystalline cellulose to amorphous cellulose would have to take place, and in doing so would make available new end groups. To date there are no experimental data to support this process.

In a recent publication, the results of the alkaline degradation studies at both low (20°C) and high temperature (90°C) have been extended to cover longer times (up to 12 years at 20°C) [12]. It is clear that the data does not fit with the earlier two phase model [8] and at 90°C there is a definite stopping of cellulose degradation [12] supporting the three-phase model outlined above and suggesting that mid-chain scission is being inhibited by the crystalline regions of cellulose. Data collected at 20°C does not demonstrate a stopping of cellulose degradation and the authors suggest the other undefined reactions maintain cellulose degradation at these extended timeframes [12] (Figure 8) such as the transformation of crystalline to amorphous cellulose. It is important to realise that the time span of these extended reactions is still along way from that of the expected life of the repository. However, it is not clear from the data presented whether this extended period of cellulose degradation is real or what is being observed is a gradual stopping of degradation similar to that seen at 90°C. The latter being in line with the three phase model described above.

### 3.2.1 Chemical Degradation of Hemicellulose

The cellulosic components of ILW and LLW will include hemicelluloses which will be soluble under alkaline repository conditions. The alkaline hydrolysis of hemicellulose components such as glucomannans and galactoglucomannans, which are constructed from isomeric aldohexoses, will generate the same degradation products as cellulose i.e. ISAs with a small amount of short chain fatty acids. In contrast, the alkaline hydrolysis of xylans has been shown to generate 3-deoxy-2-C-(hydroxymethyl)-tetronic acids (xylosachharinic acid) as the major product [41]. The low molecular weight polymers are soluble under alkaline conditions and this accounts for a large rise in the total dissolved organic carbon in the early stages of degradation studies. As soluble polysaccharides, the degradation kinetic of hemicelluloses will not include the physical stopping reactions. Consequently the peeling process is expected to lead to complete degradation of hemicelluloses. When cellulose hydrolysis is studied over extended periods it is necessary to subtract initial total dissolved organic carbon content from subsequent values to model cellulose degradation over longer periods.
### 3.3 Identification of Degradation Products

The major products generated from the alkaline degradation of cellulose are the diastereomeric α-isosaccharinic acid (3-deoxy-2-C-(hydroxymethyl)-erythro-pentanoic acid, erythro-ISA) and β-isosaccharinic acid (3-deoxy-2-C-(hydroxymethyl)-threo-pentonic acid, threo-ISA). The identity of α- and β-ISA has been confirmed using a combination of analytical techniques including HPLC, NMR, GC-MS and LC-MS/MS and by comparison with standard samples [24, 42]. The mechanism for formation of the ISAs (Figure 4) is via migration of the carbonyl group of the reducing end anhydroglucose through successive enediols to C3 followed by elimination of the C4-alkoxy group to give 4-deoxy-2,3-hexodilulose. 4-Deoxy-2,3-hexodilulose is a key intermediate and participates in a benzilic acid type rearrangement to yield the ISA isomers (see Figure 4, bottom right).

In addition to the ISA isomers, a large number of small chain aliphatic acids have been detected including: formic, acetic, glycolic, pyruvic, glyceric, lactic, propionic, succinic, butyric, threonic and adipic [15, 25]. The identity of these acids was inferred by comparison of CDP peak retention times measured using high performance ion exclusion chromatography (HPIEC) and high performance anion exchange chromatography (HPAEC) with those of known standards [43]. The origin of many of these small aliphatic hydrocarbons is believed to be from the fragmentation of 4-deoxy-2,3-hexodilulose [44]. It has also been reported that 4-deoxy-2,3-hexodilulose can be converted to a variety of C4, C5, C6 mono- and di-carboxylic acids [25]. The percentages of each of the small acids are very low, but when combined, they constitute the difference between the total dissolved organic carbon and the reported amounts of ISA.

### 3.4 Factors Controlling Cellulose Degradation Rates

The early literature, related to the influence of pH and Ca$^{2+}$ ion concentration on the degradation rates of cellulose has been reviewed by Van Loon and Glaus [8]. At hydroxide concentrations, equivalent to those found in alkaline cement waters, the rate of degradation of cellulose is independent of hydroxide concentration [45]. However Ca$^{2+}$ ions present in cement derived waters catalyse the benzilic acid rearrangements leading to both isosaccharinic acid and metasaccharinic acid and the rates of both the peeling and chemical stopping reaction are enhanced. The overall effect of an increase in Ca$^{2+}$ ions is to reduce the degree of the alkaline degradation of cellulose through increasing the rate of the stopping reaction when compared to the rate of the peeling reaction.

The effect of temperature on alkaline degradation of cellulose was first investigated by Haas et al. [46] who measured the effect of temperature on the rate constants for the peeling and stopping reactions (both the chemical stopping reaction and the physical stopping reaction). Measurements were performed between 65°C and 132°C, utilised cotton based cellulose with a DP of 160 and rates were measured in 1.25M NaOH solution. Van Loon and Glaus [8] used this rate data to calculate activation parameters and rate constants for 25°C. The activation parameter for the peeling reaction was determined to be greater than that for stopping reactions, indicating that the extent of degradation would be greater at higher temperatures. Experiments performed at 25°C, 60°C and 90°C [26, 36] identified inadequacies in the extrapolated data. The extrapolated rate constants for mid-chain scission were too low to account for the rapid degradation observed in the early phases of cellulose degradation. The failure to observe complete degradation over extended periods was attributed to a subsequent reduction in the rate of mid-chain scission as the amount of amorphous material was reduced.

### 3.5 Microbial Cellulose Degradation

The microbial degradation of cellulosic materials is a well-defined process which can lead to the generation of gases and soluble organic compounds within radioactive waste disposal sites [27]. Under the anaerobic conditions expected to dominate during the post closure period of a disposal
site, the microbial degradation of cellulose involves a wide variety of microbial groups which
ultimately result in the generation of gases such as H₂, CO₂, CH₄ and H₂S and soluble organic
compounds such as volatile fatty acids [27, 47] (Figure 6). Micro-organisms are ubiquitous in
terrestrial environments and their presence within a disposal site is inevitable [17, 48]. However,
the survival and activity of these micro-organisms will be dependent on the prevailing chemical and
physical conditions [17, 48]. Within the repository, high pH, elevated temperatures, low water and
nutrient availability will all contribute to minimising microbial activity [17, 48]. It is recognised
however that the chemical environment within the repository will not be uniform and it is likely that
niches will exist within the waste where micro-organisms may be active [17, 48]. Where favourable
niches are available for microbial growth, microbial activity can be expected to quickly establish
and may modify the local environment to increase the size of the niche e.g. by the reduction of pH
through the generation of organic acids. Studies under simulated repository conditions [48] have
demonstrated the survival (not growth) of some bacteria at elevated temperatures and a wide
range of pH values up to pH 12, with survival at temperatures as high as 90°C being enhanced
through attachment to surfaces. Survival at high pH (pH 12) being more prevalent at temperature
below 55 °C [48]. Previous estimates of repository temperatures post closure have suggested that
they may be as high as 80°C [4]. More recent estimates of peak temperature indicate that 60°C is a
more likely value with this peak temperature falling to 35°C after 10 years and 30°C after 100 years
[49] (Table 2). This temperature profile indicates that after about ten years the repository
temperatures would be within the temperature range of a large variety of micro-organisms, some of
which may be able to survive the prevailing pH.

Within the GDF concept [3] there may be a considerable time period between waste generation
and packaging and final disposal within a repository. During this period, waste packages will be
placed in interim surface storage (50 years) followed by monitored retrievable storage which may
last several hundreds of years prior to closure of a GDF [3]. Most ILW destined for disposal will
have been encapsulated using grout within suitable waste containers designed to contribute to the
physical containment of the waste [3, 50]. Other waste streams will be supercompacted rather than
encapsulated and some of these waste streams (e.g. plutonium contaminated material , PCM)
contain relatively high proportions of organic material including cellulosics such as paper, cotton
and wood [50]. Initially, in both types of waste package, microbial activity will be constrained by
water activity since free water will be limited [50]. Water activity has a major impact on microbiology
with even the most specialised organisms being inhibited once water activity drops below 0.6 [17,
51]. During retrievable storage, the relative humidity will be maintained below 60% [2] which will
help to maintain a low water content within the waste. Although grouted waste will come into
contact with grout pore waters the amount of free water available to the microorganisms is likely to
be limited. Consequently microbial cellulose degradation during storage is likely to be limited
providing the initial waste is dry and or grouted. In supercompacted waste extensive water ingress
is likely to be limited by the density of the waste [50] and any water present in the waste prior to
compaction is likely to have been released during the compaction process. Given the heterogeneity
of the waste, it is not possible to rule out niches within the waste where conditions may be
favourable for microbial activity, but these are not expected to be extensive.

Water activity will continue to control microbial cellulose degradation after backfilling and closure
until groundwater ingress into the waste takes place. Resaturation is expected to begin shortly after
closure and estimated resaturation times range from tens of years to tens of thousands of
years [49] (Table 2). Equilibration with Ca(OH)₂ is expected to maintain a pH above pH 12.0 for
tens of thousands of years until leaching allows evolved cement phases dominate the system and
the pH falls continuously beyond 100,000 years when the dissolution of CSH gels generates an
ambient pH of 10.5 [49, 52]. Anaerobic cellulose degrading bacteria able to live at high pH have
been described [17, 53, 54]. These so-called alkaliphiles appear to operate at a pH around pH 10
[55, 56]. Alkaliphilic bacteria, able to operate up to a pH of pH 12, have been described but there is
some dispute as to accuracy of these reports [57]. Consequently the bulk pH is likely to be too high
for extensive microbial cellulose degradation to occur for tens of thousands of years post closure.
During this period cellulose degradation will proceed via the chemical and radiolytic routes. Best
estimates indicate that this route may have degraded over 60% of the cellulose by ten thousand
years and 100% by one hundred thousand years [49]. These estimates suggest that the bulk of the
cellulose inventory will have degraded chemically before the pH is low enough to allow significant
microbial cellulose degradation, however any CDP present in the repository may be subject to microbial degradation.

Although the bulk pH will be too high for extensive anaerobic microbial cellulose degradation the presence of niches within the waste cannot be ruled out. Within these sites, provided sufficient water and nutrient are present, microbial degradation may proceed. Since some of the degradation products of anaerobic cellulose degradation are organic acids it is possible that microbial activity will generate low pH niches within the waste [50], this is particularly likely in supercompacted wastes.

Direct microbial cellulose degradation within the disposal system will be dependent on a range of factors such as water and nutrient availability, temperature and pH. As the disposal system re-saturates and the temperature declines towards 30°C the likelihood of direct microbial cellulose degradation increases. This is more likely to occur in the supercompacted non-grouted wastes. In the grouted wastes chemical and radiolytic cellulose degradation is likely to dominate with microbial activity being focussed on the degradation of CDPs.

3.6 Radiolytic Cellulose Degradation

There are no integrated studies investigating radiolytic and chemical cellulose degradation under conditions relevant to cellulose degradation in a geological disposal setting. Consequently any conclusions regarding the relationship between these processes have to draw from the disparate range of data available. Early research in this area focused on the effects of gamma radiation on cellulosic materials where the dominant process is mid chain scission [31, 32, 58]. Similar degradation mechanisms have been observed in cellulose irradiated by electron beam [59] but data on the effects of alpha radiation appear to be limited to gas evolution measurements carried out on plutonium contaminated wastes in the USA [60].

Chain scission has been demonstrated by the fact that dry cellulose irradiated in a nitrogen atmosphere [61] generated a series of sugars ranging from cellobiose to celloheptose. These observations are consistent with chain scission occurring at the glycosidic link between the glucose units. However, radiolytic degradation of cellulose is not restricted to cleavage of the glycosidic link. Glucose units can also undergo direct degradation forming carbonyl and carboxylic groups with the associated evolution of hydrogen, carbon dioxide and carbon monoxide [62].

Detailed speciations of the degradation products from irradiated cellulose are limited. In the case of cotton cellulose irradiated in oxygen-rich and inert environments, mixtures of acetaldehyde, acetone, arabinose, deoxy saccharides, formaldehyde, formic acid, glucuronic and gluconic acids, glucose, malonaldehyde, oxalic acid and xylose were generated [63]. No changes were observed in the qualitative composition of the radiolysis products formed in oxygen-rich or inert atmospheres, although the presence of oxygen increased the yield of all of these products, particularly of formic acid and malonaldehyde. These observations show that gaseous environment has little effect on the speciation of the degradation products of irradiated cellulose but the presence of oxygen can increase product yield.

While the chemical degradation of cellulose is influenced by the physical structure of the polymer, e.g. crystallinity, the penetrating power of gamma rays means that ionisation, radical formation and the resulting degradation occur uniformly throughout the polymer. For the less penetrating forms of radiation (e.g., α and β), degradation would be expected to be heterogenous and dependent on the radiation energy. In the case of α-radiation, for example, radiolysis is likely to be restricted to a surface layer of about 30µm thickness.

Radiation-induced chain scission in cellulose results in a reduction in molecular weight, an increased solubility, lower viscosity and the degradation of the mechanical properties. Early work by Charlesby [64] has shown that the reduction in intrinsic viscosity of gamma irradiated wood pulp and cotton linters associated with chain scission has a direct dependence on radiation dose and developed a theoretical relationship:
\[ \log \eta = -\log(R + R_o) + k, \]

Where:

- \( \eta \) is the intrinsic viscosity of the cellulose;
- \( R \) is the radiation dose;
- \( R_o \) is a virtual dose required to produce the initial number average molecular weight of the cellulose; and
- \( k \) is a constant.

A logarithmic plot of this relationship produces a straight line; this implies that during gamma irradiation, chain scission occurs uniformly through the material in both the amorphous and crystalline regions.

As many of the generic molecular properties of polymers are related to the intrinsic viscosity (e.g., degree of polymerisation), the changes in the molecular properties of irradiated cellulose can be interpreted in terms of Charlesby's relationship (Equation 3). In addition, Park has developed a similar expression for the generic molecular properties of irradiated, purified cotton [65]:

\[ \ln P = k \ln(N_n) + K, \]

where:

- \( P \) is a molecular property of the cellulose;
- \( N_n \) is the radiation dose; and
- \( k \) and \( K \) are constants.

In addition to changes in the molecular properties, the absorbed radiation dose will influence the number of chain scissions that occur and therefore the concentration of reactive end groups which could be quantified if a well characterised, consistent G-value can be determined. The G-value is defined as the number of molecules or radiolysis products that are generated per 100 eV of radiation energy absorbed. G-values, however, may not always be constant over a specific range of radiation doses and factors such as dose rate, radiation environment and polymer morphology can affect these values ([60]. Kusama and co-workers [66] have reported different G-values for main chain scission for different forms of cellulose irradiated in vacuum and under humid conditions. They also reported that the G-value for main chain scission varied for different doses in polynosic rayons and suggested that preferential degradation occurred in the amorphous phase of cellulose in the primary stages of radiolysis. Therefore there could be some doubt to the validity of equations 3 and 4 for cellulosics of different morphologies over wide radiation dose ranges, different environments and at different dose rates. The linear energy transfer (LET) of the radiation also appears to have an effect on G-values as reported in reference [60]. Here G-values for total gas generation from high LET alpha radiation in contact with cellulose were approximately 1 whilst the corresponding G-values for gamma radiation ranged from 4 to 10.

Experimental studies have confirmed that exposure of cellulose to radiation reduces the proportion of recalcitrant highly ordered material (i.e. crystallinity) [61] and also increases the susceptibility of cellulose to subsequent alkaline degradation [67]. This was confirmed in one study when the combined effects of an alkaline environment and radiation on the crystalline phase of paper tissues were examined [10]. This combination produced high levels of dissolved organic species and complexing agents but the nature of these products was not characterised. These results confirm the expected synergy between the radiation and alkaline degradation, because the levels of organic species generated by alkaline degradation alone were very much lower (~10 ppm compared to 600 ppm when irradiated). In these experiments, where a dose of ~230kGy was applied, 10% of the crystalline cellulose present was completely degraded. Given the higher accumulated doses associated with long term waste storage and disposal it is likely that a significantly higher proportion of the crystalline cellulose present will be degraded. This will provide a continued source of active sites for alkaline degradation processes which would normally be suppressed by stopping reactions.
A wide range of experimental and validation test data has resulted in the development of a successful predictive model that incorporates the synergy between thermal and radiation degradation mechanisms in polymers [68]. These empirical relationships [68] relates the time required to reach a specific level of polymer degradation to thermal degradation (Arrhenius law) and radiation degradation (as a power law). Using a similar approach, it may be possible to model the synergy between chemical degradation and radiolysis in cellulosics by using the relationships in equations 1-4. It has been shown, however, that there could be some doubt in the validity of equations 3 and 4 for different radiation conditions. Consequently any attempt to model this synergy would require experimental data to validate these equations over the environmental conditions of interest.

4 Stability/Degradation Behaviour of ISA and other CDPs under Repository Conditions

4.1 Chemical Degradation

Investigations into the chemical stability of ISA have been carried out and reviewed [12, 14, 43]. Hurdus and Pilkington [14] carried out experiments at both room temperature and 80°C over 10 and 12 months respectively. Their results indicated that the chemical degradation of ISA only occurred in the presence of oxygen; acetic, lactic and formic acids were identified as degradation products. Similar results have been presented by Glaus et al. [12] who showed ISA degradation only occurred in the presence of stoichiometric amounts of oxygen or a similar oxidant. The decomposition products were identified as a mixture of glycolic, formic and lactic acids [12]. The authors concluded that the oxidative decomposition of ISA could not be included as a process of significance in reducing the concentrations of degradation products considered in the safety assessments of repositories [12] due to limited period of oxidising conditions expected.

4.2 Microbial Degradation of ISA and other CDPs

Although α- and β-ISA are the major degradation products of alkaline degradation of cellulosic material under simulated repository conditions [25, 47, 69], a range of other organic acids are also generated including formic, lactic, acetic and propanoic acids [15]. Many of these acids are common products of microbial fermentation reactions [18, 28] and can be found in a range of anaerobic environments such as landfill sites, anaerobic digesters and sediments. The degradation of these products within anaerobic environments depends on methanogenic and acetogenic bacteria [18, 70] (Figure 6) or bacteria which couple the oxidation of these compounds to the reduction of terminal electron acceptors such as ferric iron or sulphate [17, 18, 53, 70]. Under repository conditions the degradation of these acidic, short chain organic molecules may be inhibited by pH. Considering that the repository pH is expected to be greater than pH 11.0 for hundreds of thousands of years [52] (Table 2), the removal of these non ISA containing CDPs will depend on the adaptation of the micro-organisms present in the repository to the high pH environments or their growth within biofilms or low pH niches within the waste. The removal of volatile fatty acids in alkaline environment such as soda lakes has been described [53] indicating that the removal of these compounds may be possible under repository conditions.

Bacteria able to degrade ISA under aerobic and denitrifying conditions [18, 71, 72] have been found in a range of environments with both the α- and β-isomers of ISA being degraded [18]. These bacteria were isolated at 25°C and pH 10.5 from naturally occurring alkaline sites such as the Crater and Elmenteita Lakes in Kenya, Mono Lake in the USA and samples of wood removed from Crater Lake [18] (Table 3) provided the most effective ISA degraders. This reflects the fact that these bacteria have evolved in environments where low levels of ISA are naturally present [18]. In
addition ISA degraders have been isolated from sites contaminated with industrial effluents containing ISA e.g. the Sodra Site in Sweden and materials likely to generate alkaline conditions [18] (Table 3).

The study of the Sodra site in Sweden demonstrated that ISA-degrading bacteria could evolve relatively quickly once ISA becomes available. Sodra soil samples were taken from areas that had been regularly contaminated with Black Liquor over a period of 10-15 years. Only those areas directly associated with contamination yielded ISA-degrading organisms. Samples of soil taken at distances of 1.5m, 4.2m, 9.75m, 15.45m and 46m (control) from the area of contamination did not contain any culturable ISA degraders [18]. These results suggest that the normal soil population had evolved to degrade ISA in areas where ISA represented a significant proportion of the available organic carbon. As part of the same study, attempts to isolate ISA degraders from uncontaminated soils, compost and anaerobic digester sludge were unsuccessful [18]. Since the microbial populations of these sites are likely to more closely resemble those present in the repository at closure (e.g. on soil and dust particles), it is likely that the repository will start with a largely non-specialised microbial community where the ability to degrade ISA is either absent or very limited. Results from the Sodra site in Sweden, however, suggest that these initial microbial communities may evolve the ability to degrade ISA relatively quickly provided that the conditions allow microbial activity.

Grant et al. [18] also carried out more detailed studies on ISA degrading isolates demonstrating ISA degradation between pH 7.0 and pH 11.5, with an optimum between pH 9.0 and 10.0. Further studies using Nirex reference vault backfill (NRVB) material suggested the maximum pH for ISA degradation could be as high as pH 12.5. Bacteria showing the highest pH tolerance were derived from industrially-contaminated sites that are calcium dominated rather than the sodium dominated soda lakes. These calcium dominated environments more closely resemble repository conditions than the soda lakes, suggesting that ISA degrading bacteria able to withstand pH values representative of backfilled repository may evolve within the repository. ISA degrading biofilms were also investigated by Grant et al. [18] who were able to establish viable biofilms on both NRVB and concrete surfaces. ISA degradation rates for bacterial suspensions ranged from 0.2 to 5.6 mol ISA yr^{-1} g^{-1} whereas biofilms removed ISA at between 40 and 350 mol ISA yr^{-1} m^{-2} of surface area. These microbial cultures were able to reduce ISA concentrations from 10^{-2} M to below 10^{-4} M.

As noted above, the aerobic microbial degradation of ISA has been described by a number of authors [71, 72]. The ISA degrading isolates described by Grant et al. [18] coupled ISA degradation to nitrate reduction (denitrification) with the concurrent oxidation of ISA to carbon dioxide. The coupling of ISA oxidation to more reduced terminal electron acceptors, such as sulphate, remains to be demonstrated and the degradation of ISA by methanogenic microbial communities has not been shown. However the successful treatment of Kraft pulp mill effluents by anaerobic treatment systems [73] suggests that ISA degradation under methanogenic conditions may be possible. Likewise Maset et al. [74] demonstrated that at neutral pH soil microbial communities can degrade ISA under a wide range of environmental conditions without the need for an adaptation period.

Current understanding indicates that aerobic microbial populations in soil can adapt in a few decades to degrade ISA when it is the dominant carbon source. Bacteria isolated from these sites can also degrade ISA in the absence of oxygen by using nitrate as a terminal electron acceptor [18]. This suggests that although ISA degrading micro-organisms may not be active when a repository is closed, a mixed population could develop as ISA becomes the dominant carbon source within the system through the chemical hydrolysis of cellulose. This hypothesis assumes that microbial ISA degradation under strongly reducing conditions is as prevalent as has been demonstrated under aerobic and denitrifying conditions [18, 71, 72]. Such organisms will grow preferentially in niches where the pH values between 9 and 10, the optimum pH for ISA degradation reported by Grant et al. [18]. The maximum pH for ISA degradation reported by Grant et al. [18] being 11.5. Therefore, biofilms may be particularly important for the survival and activity of ISA degrading bacteria under high pH conditions seen within the repository (Table 2). These ISA degrading communities may then degrade ISA at a rate that may contribute significantly to the removal of ISA from repository pore waters. The impact of these communities may be attenuated
by the availability of nutrients such as nitrogen and the possible absence of terminal electron acceptors such as nitrate.

4.3 Radiolytic Degradation of CDPs

Exposure of CDPs to ionizing radiation is expected to induce their decomposition by chain scission to even lower molecular weight species and gas (decarboxylation). Data describing the degradation rates of CDPs during radiolysis are not available. However, the factors that affect the radiolysis of CDPs are likely to be the same as those that affect the radiolysis of the original cellulose material. These factors include the radiation dose rate, the chemical nature of the CDPs, the chemical environment and the irradiation temperature. Data on the chemical stability of ISA indicate that ISA is stable in the absence of oxygen [12] or other oxidising agents suggesting that potentially oxidising conditions generated by radiolysis could play a role in the removal of ISA from the near field of a repository. Confirmation of the impact of radiolysis on near-field complexant concentrations would be beneficial.

4.4 Solubility and Sorption of ISA and CDPs

The solubility and sorption of CDP onto repository components such as cement, grout and backfill material may have a significant impact on the migration of CDPs from the repository and their ability to enhance radioelement migration [4, 52]. Although CDPs are a mixture of materials [14, 75] sorption studies have concentrated on the behaviour of α-ISA [11, 14] and there is evidence that the sorption properties of the two isomers are similar [8, 11]. The sorption behaviour of ISA is not strongly dependent on the type of cementitious material concerned [6, 8, 11, 14, 49], rather it is determined by the calcium-silicate-hydrate and calcium-aluminium-silicate-hydrate phases present [8]. Experimental data on ISA sorption [6, 14, 76] indicate that R_d values for ISA begin to fall as the initial ISA concentration increases beyond a values of 0.01 mol dm^{-3}.

In addition to sorption, ISA precipitation as a calcium salt will also moderate the concentration of ISA in the near-field [8, 14]. In this case there are significant differences in the solubilities of the two ISA isomers with β-ISA being significantly more soluble than α-ISA [8, 14]. Experiments using NRVB measured α-ISA concentrations of 0.05M in the presence of calcium α-ISA salt [14]. This value is in agreement with experimental and modelled results published by Van Loon and Glaus [8] for cement pore waters in the early stages of cement degradation when the pH is in the region of pH 13 due to the presence of alkali metal hydroxides. When cement pH becomes dominated by Ca(OH)_2 dissolution, after the leaching of the alkali metals, the pH drops to pH 12.5 and a maximum solution α-ISA concentration of around 0.02M is predicted [8]. In view of these data, Van Loon and Glaus [8] concluded that calcium ISA precipitation would not be sufficient to reduce the impact of ISA on radioelement complexation in the Swiss disposal context.

5 CDP Migration - Persistence of CDPs in the Geosphere

The fate of ISA and associated CDPs in the geosphere is determined by a range of inter-related processes such as microbial and chemical degradation, precipitation and sorption. The nature and extent of these processes will depend on the relative geochemical characteristics of the geosphere and the intruding plume. As the plume moves out from the repository, dilution and dispersion will have a significant impact on the concentration of CDPs in the geosphere [4]. These processes will also reduce the chemical impact of the plume, with the plume pH and Eh being modified until they eventually match that of the host rock.

In the geosphere microbial degradation processes will be determined by the prevailing geochemistry and mineralogy since they will be dependent on the availability of terminal electron acceptors. A review of available literature indicates that ISA degradation under geosphere conditions has not received significant study with research focusing on degradation under aerobic
and near-field conditions [18, 72]. To date, microbial degradation of ISA has only been confirmed under aerobic and denitrifying conditions [18, 72] (Section 4.2), although its degradation under more reduced environmental conditions seems likely [18]. In the deep subsurface surrounding a repository, oxygen and nitrate are unlikely to be present in significant quantities, unless waste-derived nitrate is a component of the near-field plume. Microbial terminal electron acceptors more common in the geosphere are manganese(IV), ferric iron and sulphate; in addition, fermentation processes and methanogenesis are also possible [70, 77]. ISA oxidation coupled to manganese, iron and sulphate reduction will result in the complete oxidation of ISA to carbon dioxide with the generation of the associated reduced manganese, iron and sulphur species. In the absence of these terminal electron acceptors anaerobic degradation of ISA with the associated generation of methane may occur. Data from environments contaminated with ISA suggest that microbial communities are able to adapt to ISA degradation relatively quickly in comparison to the timescales considered in repository performance assessments [18]. The majority of non-ISA CDPs are common microbial substrates such as volatile fatty acids [15, 18, 28] and are therefore likely to be degradable under geosphere conditions [18, 28, 70]. Until possible candidate sites are identified, geosphere specific research on microbial ISA degradation to enable predictions of degradation rates is not possible.

Chemical degradation of ISA appears to require oxygen or a similar oxidant [12], consequently chemical degradation is unlikely to occur in the geosphere until the plume reaches the near surface/oxidising layer [52]. The amount of CDPs reaching this point will be determined by dilution and dispersion and the extent of microbial degradation and sorption to rock surfaces that occurs along the flow path.

6 Treatment of Cellulose Degradation in Performance Assessment

The treatment of cellulose degradation in performance assessments for the geological disposal of long-lived radioactive wastes in the UK falls in two areas. First, its role in gas generation processes [78, 79] and secondly its enhancement of radionuclide migration in groundwater due to the generation of complexants such as ISA [47]. The treatment of the impact of CDPs on radionuclide migration is dependent on the treatment of a number of underlying processes:

- the extent and rate of cellulose degradation in the near-field with time;
- the persistence of the resulting CDPs in both the near-field and on migration into the geosphere; and
- the sorption of CDPs onto near-field and far-field components.

This section focuses on the treatment of cellulose degradation processes in assessments of the groundwater pathway which underpins the treatment of the impact of CDPs on radionuclide migration. The treatment of the latter in previous assessments in the UK is outlined in Appendix 1 [4].

6.1 Developments in the Treatment of CDPs in Performance Assessments

The consideration of cellulose degradation in performance assessment has focused on the ability of CDPs to influence the transport of radionuclides through their impact on the solubility and sorption of radionuclides. This impact is simulated by assigning a solubility enhancement factor (SEF) and sorption reduction factor (SRF) for each radionuclide [4] (Appendix 1). Existing performance assessment calculations [80-83] (see Appendix 1) do not include an explicit consideration of repository evolution. However, it is captured in the elicitation of the uncertainty in radionuclide solubility and sorption parameters. Since the generation of CDPs could have an important impact on repository performance the representation of an evolving cellulose inventory is
a potentially important enhancement. Log triangular probability density functions (PDFs) describing the evolution of the extent of cellulose degradation were first described by Chambers et al. [84], along with the first elicitation of SEFs and SRFs expressed as a function of cellulose loading (cellulose loading being calculated by dividing the mass of cellulose by the total mass of cellulose plus backfill). Cellulose loading can then be correlated with the extent of cellulose degradation allowing SEFs and SRFs to vary as the extent of cellulose degradation increases with time. The work reported by Chambers et al. [84] was updated by Chambers and Williams [11] who reviewed the PDFs for cellulose degradation with time, and radioelement SEFs and SRFs. In addition they derived PDFs for the sorption of CDPs onto cement to allow the removal of CDPs from the near-field via groundwater flow to be considered (Table 4). A pragmatic approach to the derivation of SEFs and SRFs as a function of the pore water concentration of CDP was also developed [11]. This was proposed as an alternative to linking SEFs and SRFs to cellulose loading since it makes a more direct connection between the extent of cellulose degradation and its impact on radioelement chemistry [11].

6.1.1 Review of Cellulose Degradation PDFs

PDFs for the extent of cellulose degradation with time were reported by Chambers et al. [84] following an expert elicitation process. These PDFs were reviewed and revised by Chambers and Williams [11] in the context of data from alkaline cellulose degradation experiments carried out by Glaus and Van Loon [26]. Initial log triangular PDFs (Figure 9) [84] were derived assuming that the cellulose inventory could be split into reactive or amorphous cellulose (10%) which degrades rapidly (<1 year post closure) and crystalline or recalcitrant cellulose which degrades much more slowly and was the focus of the elicitation exercise. Chambers and Williams [11] point out that published data [26] derived under conditions (60°C and pH 13.3) close to those expected in a UK repository (Table 2) indicate that reactive amorphous cellulose accounts for closer to 35% wt of the cellulose rather than the 10% previously assumed [84]. Based on this observation Chambers and Williams [11] recommended that in future performance assessments the amount of reactive amorphous cellulose should be assumed to account for 35%wt. This would also allow for the potential generation of amorphous cellulose from crystalline cellulose during storage due to radiation effects and the impact of aggressive chemical such as hydrochloric acid. Basing this modification on the available experimental data does assume that the cotton cellulose used in these experiments is representative of the cellulosic wastes likely to be present in a UK repository. This assumption is unsupported and it should be noted that cellulose from different sources can have very different characteristics such as DP and crystallinity [19], it might be better in future to correlate cellulose degradation rates to physical characteristics of the material rather than its origins, however, the practicality of this approach would require testing.

Revised cellulose degradation profiles including increased estimates of reactive cellulose were produced by Chambers and Williams (Figure 10) [11], which also include the impact of radiolysis on cellulose degradation [10]. The main changes to the profiles are the bringing forward of the upper bound and best estimate times for significant degradation of recalcitrant cellulose reflecting the inclusion of radiolytic degradation into the elicitation process. The upper bound values after 1 year were significantly increased to reflect the rapid rates of Aldrich cellulose degradation published by Glaus and Van Loon [26]. This rapid degradation may reflect the low DP of the Aldrich cellulose (DP ~120) used and may not be reflective of the reactivity of the paper and wood cellulosic material present in the repository. The other major change to the total cellulose degradation profiles (c.f. Figure 8, Figure 9 with Figure 10) is a significant increase in the extent of degradation up to and including 10,000 years, which reflects the increased estimate (from 10%wt to 35%wt) of the proportion of reactive amorphous cellulose and reflects the impact of radiolysis.

The cellulose degradation profiles generated by Chambers et al. [84] and reviewed by Chambers and Williams [11] were informed by modelling studies using two models; GAMMON [84] and the PSI model described by Van Loon and Glaus [8, 40]. Both of these models simulate alkaline cellulose degradation via the cumulative impact of peeling, stopping and mid chain scission reactions [8, 40, 84]. Recently published work carried out by Glaus et al. (2007) [12] investigated the alkaline degradation of cellulose over time periods up to 12 years. This work represents the most extended investigation to date on alkaline cellulose degradation. Glaus et al. (2007) [12]
concluded from this and related work [26] that current mechanistic models like those used to inform the elicitation process reported by Chambers et al. [84] were only useful when modelling time periods of several hours and that other undefined reactions became dominant at extended timescales. These discrepancies between existing models and experimental data were particularly pronounced at moderate temperatures (e.g. 60 and 90°C) [12]. The authors suggest that this disagreement between modelling and experimental data indicates that modelling studies can overestimate the stability of cellulose over 1000s to 10,000s of years [12], largely due to the absence of reactions which maintain the long term alkaline degradation of cellulose [12]. Although it should be noted that these processes are often included during the expert elicitation process [11, 84].

The conclusions drawn by Glaus et al. (2007) [12] suggest that a modification may be required to the best estimate and lower bound values for cellulose degradation to reflect the proposed increase in long term degradation. A possible modification to the existing PDFs is shown in Figure 11. However, given the uncertainties surrounding the as yet undefined reactions that are proposed to maintain the long term degradation of cellulose [12], formal revision of the existing PDFs is not proposed until further information is obtained supporting the operation and impact of these proposed reactions as well as the impact of radiation effects. In addition, further data concerning waste cellulose characteristics would be of benefit to inform the elicitation of the reactive cellulose fraction.

7 State of the Art

7.1 Chemical and Radiolytic Degradation

The current models for the mechanism of alkaline hydrolysis of cellulose involve three reaction phases: an initial rapid degradation in which the peeling of end groups dominates; a slower second phase of cellulose degradation in which mid-chain scission releases new end groups that can participate in the peeling process; a third final phase when stopping reactions dominate as the amount of amorphous material containing available end groups reduces. The key features of the proposed mechanism is that the degree of degradation of cellulose and the resulting production of ISAs and CPDs will be high in the first phase, equivalent to the degradation of less than 25% of the insoluble cellulose [26]. The second phase will lead to further degradation of cellulose but a lack of suitable data and uncertainty in the rates of mid-chain scission at room temperature make predictions of the extent of degradation and calculations of the concentration of ISA produced uncertain. Further work could be undertaken in an attempt to rationalise the measured rates of mid-chain scission observed at elevated temperature with the much lower rates observed at 25°C. There are reports in the recent chemical literature for the spontaneous hydrolysis of glycosides [85]. Although these processes will be very slow at 25°C, there is a possibility for Ca$^{2+}$ catalysis and this could be explored.

In this three-phase model, the rate of mid-chain scission reduces to zero as the amount of accessible amorphous material decreases (Figure 8). For mid-chain scission to continue the transformation of crystalline cellulose to amorphous cellulose would have to take place. At present there is uncertainty as to whether or not this process maintains cellulose degradation at a lower rate over extended time periods. Some authors have proposed a set of as yet undefined reactions [12] which do allow prolonged cellulose degradation at low temperature. However, it is not clear from the data presented whether there is in fact an extended period of cellulose degradation or a gradual stopping of degradation [12]. The experiments would need to be run for a longer period to establish which of the two scenarios is accurate, however it is recognised that there are issues with running and maintaining experiments over decades. It would also be useful for a range of intermediate temperatures to be investigated e.g. 20, 30, 40, 50°C to allow a more systematic assessment of the impact of temperature to take place. These experimental programmes should include the impact of radiation doses consistent with that likely to be present with in a disposal system.
The identity of the major degradation products formed during alkaline hydrolysis has been established. The major degradation products are the $\alpha$- and $\beta$-ISAs and the time course for their formation can be monitored using high performance anion exchange chromatography a technique that is now routinely applied for the quantification of carbohydrate based analytes. The identity of a range of small fatty acids which contribute to the remaining TOC has also been established, for a review of the subject see Knill and Kennedy [25].

The current understanding of the fate of the degradation products comes from work by Hurdus and Pilkington [14] and Glaus and Van Loon [43] who have analysed the chemical stability of CPDs: it is clear that in the absence of an oxidant CPDs are stable in the short term. Further studies, at elevated temperatures, of the alkaline stability of ISAs are needed to be able to predict their long-term stability.

The vast majority of the work that has been performed on the alkaline hydrolysis of cellulose has used changes in product concentrations to monitor the degradation process. There have been very few studies that have looked at changes in the starting material during the course of the reactions. Modern analytical techniques are routinely applied to the study of bulk properties of solid polysaccharides; important questions need to be asked with regard to the change in structure of the starting materials with time. Important questions relate to how the DP, degree of crystallinity, the type of crystallinity and the number of available end groups change as the reaction proceeds. NMR and atomic force field spectroscopy could be used to monitor the degradation of cellulosates of known structure.

A significant amount of information is available in the literature that describes the radiolysis of cellulose by gamma and electron beam irradiation. A significant amount of this information is associated with the processing of cellulose for enhanced biodegradation or the production of ruminant feedstock. This is a much reduced body of information available regarding the effects of radiation on the cellulosic materials that would be expected to be present in ILW streams. There is currently a lack of detailed information regarding the relationship between radiation and alkaline degradation, for example, the synergy between high pH environments and radiation, enhancement of alkaline degradation after irradiation and the radiolysis of CDPs. Given that the stability of CDPs appears to be dependent on the presence of oxygen or oxidised species [12], radiolytic effects could play an important role in reducing the near-field concentration of CDPs through the generation of free radicals.

There has been no systematic attempt to relate the physical nature of the inventory cellulosic materials (DP, crystallinity, number of available end groups) with their reactivity under repository conditions. This has led to experimental data derived on one cellulosic material to be applied to the degradation of different cellulosic materials under repository conditions. Likewise little work has been carried out to determine the combined effects of alkaline cellulose degradation and radiation effects on the overall rate and magnitude of cellulose degradation. Some attempt to identify the degradation characteristics of the individual cellulosic materials (wood, paper, cotton, etc) present in the repository and the impact of radiation effects would help to increase confidence in the representation of cellulosic materials in performance assessments.

### 7.2 Microbial Degradation

Under simulated repository conditions [86], bacteria have been shown to survive at elevated temperatures and a wide range of pH values, with survival being enhanced through attachment to surfaces. Indicating that bacteria present at repository closure will be able to survive within the repository even though the bulk pH is expected to stay above pH 12 for tens of thousands of years [49] (Table 2). Although anaerobic cellulose degrading bacteria able to live at high pH have been described [17, 53, 54], it is likely that cellulose degradation within the repository will proceed via the chemical route. This is because these alkaliphiles operate at a pH around pH 10 [55, 56], significantly lower than the expected repository pH [49] (Table 2). Microbial activity and cellulose degradation may be limited to niches within the repository where the pH is lower. Since some of the
degradation products of anaerobic cellulose degradation are organic acids it is possible that microbial activity will contribute to the generation of these low pH niches within the waste [50].

Bacteria able to degrade both α- and β-ISA have been isolated from a range of natural and industrially contaminated environments [18] (Table 3). Data from industrially contaminated sites indicate that the evolution of ISA degrading microbial populations can occur within decades [18]. To date however, bacteria able to degrade ISA have only been isolated under aerobic and denitrifying conditions [18, 71, 72], conditions unlikely to dominate within the near-field or geosphere of a radioactive waste disposal site. Some studies have demonstrated the degradation of ISA at neutral pH in soil systems under a wider range of conditions [74]. Detailed investigation of microbial ISA degradation under conditions relevant to the near-field and geosphere and specifically within methanogenic, sulphate reducing and iron reducing environments would improve understanding of ISA behaviour and persistence under near-field and geosphere conditions.

8 References


### Table 1. Phases of the cement-based geological disposal concept for ILW/LLW [3]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1 – Packaging the waste</td>
<td>Waste is packaged in a form that is suitable for all phases of the disposal concept, i.e. surface storage, transport, emplacement and storage underground. The packages provide the first of the multiple barriers – the main safety function being physical containment.</td>
</tr>
<tr>
<td>Phase 2 – Surface storage</td>
<td>Packaged wastes are generally stored at the site of origin in surface stores for up to 50 years. Storage conditions are designed to ensure that the waste packages remain suitable for subsequent underground storage in a phased geological repository.</td>
</tr>
<tr>
<td>Phase 3 – Transport</td>
<td>The transport of waste packages to a repository will take place in accordance with international standards.</td>
</tr>
<tr>
<td>Phase 4 – Waste emplacement</td>
<td>Waste is emplaced in deep underground storage vaults constructed in a stable geological environment able to provide geological containment. The storage environment is carefully controlled to preserve the condition of the waste packages.</td>
</tr>
<tr>
<td>Phase 5 – Monitored retrievable storage</td>
<td>The repository and its contents are subject to monitoring and the waste remains retrievable. This phase could be maintained for several hundreds of years pending a decision to close the repository.</td>
</tr>
<tr>
<td>Phase 6 – Vault Backfilling</td>
<td>Once a decision to close the repository has been made the repository vaults would be backfilled with a specially developed cement-based material. This material is designed to provide a barrier against the release of radioactive materials into the groundwater by reducing the solubility and increasing the sorption of radionuclides.</td>
</tr>
<tr>
<td>Phase 7 – Repository closure</td>
<td>When backfilling has been completed, the repository can be closed and sealed. The vaults, connecting tunnels and repository access ways would be backfilled and closed using high integrity seals.</td>
</tr>
<tr>
<td>Phase 8 – After closure</td>
<td>Although the repository is designed to provide long-term protection for human health and the environment waste without the need for continuing maintenance. Plans for very long-term monitoring of the performance of a closed repository would be implemented prior to repository closure.</td>
</tr>
</tbody>
</table>
Table 2. Evolution of the near field after closure [49, 52]

<table>
<thead>
<tr>
<th>Period (years)</th>
<th>At closure</th>
<th>1s to 10s</th>
<th>10s to 100s</th>
<th>100s to 1,000s</th>
<th>10,000s</th>
<th>100,000s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eh</td>
<td>Oxidising</td>
<td>Oxidising</td>
<td>Initially oxidising but decreasing</td>
<td>Predominantly Reducing</td>
<td>Predominantly Reducing</td>
<td>Predominantly Reducing</td>
</tr>
<tr>
<td>pH</td>
<td>N/A</td>
<td>&gt;12.4 Dominated by NaOH, KOH</td>
<td>&gt;12.4 Dominated by NaOH, KOH</td>
<td>≈12.4 Ca(OH)₂ Equilibration</td>
<td>≈12.4 Ca(OH)₂ Equilibration</td>
<td>≈11.0 Evolved Cement Phase Equilibrium</td>
</tr>
<tr>
<td>Temp(°C)</td>
<td>Ambient</td>
<td>Initially 60 but falling to ≈35</td>
<td>35 to 30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Moisture content</td>
<td>Dry, Rh 60%</td>
<td>Dry, some re-saturation possible</td>
<td>Re-saturation ongoing</td>
<td>Re-saturation Complete</td>
<td>Re-saturation Complete</td>
<td>Re-saturation Complete</td>
</tr>
<tr>
<td>Wasteform integrity</td>
<td>Waste containers intact</td>
<td>Waste containers intact</td>
<td>Some penetration via corrosion, majority remain intact</td>
<td>Container integrity lost due to corrosion</td>
<td>Container integrity lost due to corrosion</td>
<td>Container integrity lost due to corrosion</td>
</tr>
<tr>
<td>Corrosion</td>
<td>Not significant</td>
<td>Reducing oxygen levels</td>
<td>Hydrogen generation from corrosion peaks</td>
<td>Gas generation drops to a very low level at the end of this period</td>
<td>Not significant</td>
<td></td>
</tr>
<tr>
<td>Cellulose degradation</td>
<td>None. Inhibited by low water availability.</td>
<td>Limited, controlled by water availability.</td>
<td>Alkaline degradation ongoing in saturated regions</td>
<td>Alkaline cellulose degradation ongoing.</td>
<td>Alkaline cellulose degradation complete</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Isolation of ISA degrading bacteria [18]

<table>
<thead>
<tr>
<th>Source</th>
<th>Growth on ISA/yeast extract</th>
<th>ISA removal demonstrated</th>
<th>Age of site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crater Lake consortium</td>
<td>Strong growth</td>
<td>✓</td>
<td>&gt;10^3 yrs</td>
</tr>
<tr>
<td>Elmenteita consortium</td>
<td>Strong growth</td>
<td>✓</td>
<td>&gt;10^3 yrs</td>
</tr>
<tr>
<td>CS3 isolate from Crater Lake</td>
<td>Strong growth</td>
<td>✓</td>
<td>&gt;10^3 yrs</td>
</tr>
<tr>
<td>Wood from Crater Lake</td>
<td>Strong growth</td>
<td>✓</td>
<td>Unknown</td>
</tr>
<tr>
<td>Mono Lake wood</td>
<td>Strong growth</td>
<td>X</td>
<td>Unknown</td>
</tr>
<tr>
<td>Alkaline effluent lagoon. New Zealand paper pulping site.</td>
<td>Some growth</td>
<td>✓</td>
<td>8 yrs</td>
</tr>
<tr>
<td>Soil from Sodra site (Sweden)</td>
<td>Strong growth</td>
<td>✓</td>
<td>10-15 yrs</td>
</tr>
<tr>
<td>Tank of black liquor from Modo</td>
<td>Strong growth</td>
<td>✓</td>
<td>4 yrs</td>
</tr>
<tr>
<td>Alkaline soils</td>
<td>No growth</td>
<td>X</td>
<td>Wide range</td>
</tr>
<tr>
<td>Pulverised fuel ash soil mix</td>
<td>Strong growth</td>
<td>✓</td>
<td>&lt;20 yrs</td>
</tr>
</tbody>
</table>

Table 4. PDFs for ISA sorption onto aged cement [11]

<table>
<thead>
<tr>
<th>Probability</th>
<th>$K_d$ for ISA sorption onto aged cement / cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low initial ISA concentration</td>
</tr>
<tr>
<td>0</td>
<td>1.0x10^{-3}</td>
</tr>
<tr>
<td>0.1</td>
<td>3.1x10^{-2}</td>
</tr>
<tr>
<td>0.33</td>
<td>4.2x10^{-1}</td>
</tr>
<tr>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>0.67</td>
<td>5.9</td>
</tr>
<tr>
<td>0.9</td>
<td>52</td>
</tr>
<tr>
<td>1</td>
<td>1.0x10^{3}</td>
</tr>
</tbody>
</table>
Figure 1. Cement-based geological disposal concept for ILW/LLW [2, 3]
Figure 2. The structure of cellulose and related compounds
Cellulose H-bonding

Figure 3. The structure of cellulose
Figure 4. Cellulose alkaline degradation pathways leading to isosaccharinic acid and metasaccharinic acid
Figure 5. Alkaline catalysed mid-chain scission of cellulose
Figure 6. Anaerobic microbial cellulose degradation
Figure 7. Model of the alkaline hydrolysis of cellulose including peeling, mid-chain scission and stopping reactions.
Time

Peeling reaction

Mid-chain scission followed by the peeling reaction

Additional long term reactions ultimately leading to cellulose degradation via the peeling reaction

Mid-chain scission inhibited by crystalline regions of cellulose

Figure 8. Potential long term cellulose profile for chemical degradation

Figure 9. The extent of total cellulose degradation (reactive + recalcitrant) as a function of time [84]
Figure 10. Revised estimates of the extent of total cellulose degradation (reactive + recalcitrant) as a function of time [11]

Figure 11. Possible modified estimates of the extent of total cellulose degradation (reactive + recalcitrant) as a function of time
Appendix 1
Consideration of CDPs in Performance Assessment: Solubility and Sorption Considerations
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A1.1 Near-field Considerations

Initial representations of cellulose degradation in performance assessment focused on the ability of CDPs to influence the transport of radioelements out of the near-field through their impact on the solubility and sorption of radioelements. This impact was simulated by assigning a solubility enhancement factor (SEF) and sorption reduction factor (SRF) for each radioelement [A1]. SEFs and SRFs being defined as:

\[ SEF = \frac{S_{\text{org}}}{S_0}, \quad SRF = \frac{K_{d,\text{org}}}{K_{d,0}} \]

Where \( S_{\text{org}} \) is the solubility in the presence of CDPs (under a given set of conditions) and \( S_0 \) is the solubility in the absence of cellulose degradation products (under the same conditions), \( K_{d,\text{org}} \) is the sorption coefficient in the presence of CDPs (under a given set of conditions), and \( K_{d,0} \) is the sorption coefficient in the absence of CDPs (under the same conditions).

This approach gives a single SEF and SRF for each element but with no associated uncertainty. These organic factors, as the SEFs and SRFs are collectively known, are calculated by considering the average expected cellulose concentration and making a judgement regarding the extent of cellulose degradation and associated CPD production. This approach results in the rate of cellulose degradation becoming a key uncertainty in performance assessment, since it underpins the derivation of these factors and the associated calculations of radioelement migration they are employed in.

In the Nirex 95 performance assessment [A2] organic factors were based on laboratory data collected over several months. The following performance assessment (Nirex 97 [A3]) adopted a scenario based approach which allowed uncertainties surrounding cellulose degradation to be investigated. This assessment considered three scenarios:

Scenario A  All cellulosic wastes are degraded to CDPs shortly after repository closure. Organic factors were derived from experimental data, taking into account that complete degradation is not observed in the laboratory. These factors were assumed not to vary over time.

Scenario B  Based on experimental data it was assumed that approximately 10% of the cellulose inventory would degrade. Organic factors were derived solely from experimental data, assuming that the degradation in a repository would be no greater than that observed in the laboratory.

Scenario C  CDPs have no impact on radioelement behaviour because they are removed through microbial activity within the near-field on a timescale that is short compared to that considered by the performance assessment.

Scenario A was assumed to be the most likely, with Scenarios B and C treated as variants. The organic factors for each radioelement were given a single time-independent value, and no account was taken of uncertainties in the parameters used to derive the SEFs and SRFs.

For the 2001 Generic Performance Assessment [A4] the treatment of CDPs was revised [A1] to include PDFs for both the extent of cellulose degradation with time and the impact of CDPs on radioelement chemistry at a given cellulose loading. These PDFs were in the form of log-triangular distributions comprising a central value with upper and lower bounds with a log linear relationship being assumed between elicited points. Although this revision remained time independent it was based on a methodology developed to allow a probabilistic time-dependent treatment of the impact of cellulose degradation on radioelement migration [A5]. This methodology employs three stages:

1. the derivation of the uncertainties in the time evolution of the concentration of cellulose degradation products in a repository;
2. The derivation of the uncertainty in the impact of different total concentrations of complexants on the solubility and sorption of radioelements considered in performance assessments;
3. linking these uncertainties so that the uncertainty in the impact of the time-evolving concentration of cellulose degradation products on the solubility and sorption of radioelements can be represented in an assessment.

Data from solubility and sorption experiments over a range of cellulose loadings were used to derive SEFs and SRFs for the radioelements followed in the assessment. However, to accommodate differences between experimental and repository cellulose loadings and the fact that cellulose degradation may proceed to completion over repository timescales but not over experimental ones. It was assumed that the magnitude of the effect of cellulose degradation products was proportional to the product of the cellulose loading and the extent of degradation [A1]. To take into account the differing decay rates of the radioelement inventory, the degree of cellulose degradation used in assigning SEFs and SRFs was taken to be that when 99% of that radionuclide had decayed. For the 2001 and 2003 GPAs [A4, A6] this approach resulted in SEFs and SRFs corresponding to 100% degradation being assigned to all radionuclides with the exception of $^{59}\text{Ni}$, $^{63}\text{Ni}$, $^{90}\text{Sr}$, $^{137}\text{Cs}$ and $^{241}\text{Am}$.

### A.1.2 Geosphere Considerations

The assessment treatment of CDPs in the geosphere focuses on their impact on radioelement sorption. In the Nirex 95 assessment [A2] SRFs were obtained from calibration graphs compiled from available data describing the effect of cellulose degradation products on radioelement sorption onto rocks assuming a log-linear relationship. Where no direct experimental data were available the likely response of elements was determined by chemical analogy with radioelements being assigned to groups and each group being assigned an appropriate SRF. SRFs were conservatively based on the highest expected percentage of cellulose in the repository and that organic complexants would only have a significant impact in the matrix and Type I features of the BVG1 [A2]. In the Type II feature network and the overlaying sandstones it was assumed that dilution of CDPs was sufficient to ensure they did not have a significant impact on sorption. In addition it was assumed that the extent of rock matrix diffusion was reduced for complexed radioelements. The approach employed for Nirex 95 contained a number of cautious assumptions, which were adopted to overcome gaps in the available data for individual radioelements and uncertainties concerning the rates of generation and stability of CDPs. To address some of these cautious assumptions in later assessments, further experimental work was commissioned.

SRFs were again employed in the Nirex 97 assessment [A3] with three models of the impact of CDPs considered for probabilistic assessment:

- **Model S1** no organic complexants;
- **Model S2** only amorphous cellulose degrades to produce organic complexants;
- **Model S3** cellulose degrades completely to produce organic complexants.

For hydrogeological units below the sandstones, SRF were assigned to groups of radioelements for Model S2 and S3 with SRF for S1 being set to 1. Molecular diffusion coefficients and the anion exclusion factor were modified to account for the respective diffusion and exclusion of radioelements and complexes from the rock matrix.

The treatment of CDPs and their impact on geosphere radioelement migration in GPA and GPA 03 were essentially the same. In the GPA [A4] SRFs were not employed in the geosphere of the reference case because it was assumed that dilution was sufficient to ensure the impact of CDP was negligible [A1]. Variant calculations were performed using SRF in the Reference Case’s oxidising and reducing rock units. These SRF were derived from those employed in Nirex 97 [A3] by applying a simple representation of the uncertainty associated with the geosphere SRFs.

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1 Borrowdale Volcanic Group
Experimental data were only available for three elements (Th, U and Pu) and consequently the application of geosphere SRFs to elements without supporting experimental data was also reviewed. As with near-field SRFs a log-triangular distribution was used for those elements for which experimental data was available. For these elements the central values for SRFs were based on experimental sorption determinations at 10% cellulose loading and the degree of degradation achieved in the experiments.

For those elements with no experimental data, geosphere SRFs were derived as described below.

- Those chemically similar to elements within experimental data were given the same SRF as that element.
- An SRF of 1 with no associated uncertainty was assigned to those elements unlikely to form complexes with CDPs.
- For elements with no chemical analogue but with the potential to form weak complexes with CDPs. A uniform PDF was assigned between the lower limit for Th (the sorption distribution coefficient is not strongly perturbed by the presence of organic complexants) and the upper limit of 1.
- For elements with no chemical analogue and no information regarding the potential strength of CDP complexation. A uniform PDF was assigned between the lower limit for Pu (the element with the maximum effect of those measured) and the upper limit of 1.

In addition to SRFs charge/size exclusion factor was assigned for anionic and complexed forms of radioelements travelling in the reducing and oxidising regions of the geosphere. The derivation of SEFs and SRFs for previous performance assessments [A5] were hindered by a lack of available data on the impact of CDPs on radioelement chemistry for a full suite of elements [A5, A7]. Consequently the PDFs for SEFs and SRFs generated by Chambers et al. [A5, A7] were reviewed in light of further data (e.g. A15) and a revised set of SEFs, SRFs, solubilities and sorption coefficients for Pu, U(IV), U(VI), Ni, Nb, Th, Am, Np and Zr at a range of cellulose loadings were published by Chambers and Williams [A7].

A1.3 Sorption, Solubility and Stability of CDPs

To allow the evolution of near-field CDP concentrations to be incorporated into performance assessments, it was necessary to incorporate CDP sorption onto cement and other repository components [A7]. Given the uncertainty regarding the behaviour and nature of CDPs and the level of experimental data available, ISA was taken to represent CDP in the derivation of PDFs CDP sorption [A7]. It was recognised that ISA was a reasonable analogue for CDPs in the high pH of a repository, a situation which is not necessarily the case under the lower pH conditions of the geosphere [A7]. Recognising the range of cementitious materials present in the near-field, PDFs were elicited for ISA sorption onto a generic cement rather than NRVB [A7]. Log triangular PDFs were elicited for two ISA concentrations (<0.01 mol dm\(^{-3}\) and 0.1 mol dm\(^{-3}\)) reflecting the dependency of ISA sorption on its initial concentration [A7, A8] (Table 4). The quantity elicited was a sorption distribution value (\(R_d\) in units of cm\(^3\) g\(^{-1}\)) which was assumed to be equivalent to the sorption distribution coefficients (Kd) used in performance assessments. Assumptions used in the elicitation along with influencing factors and identified sources of uncertainty that would influence ISA sorption are outlined in Table A1. The PDFs derived for the ISA concentrations below 0.01 mol dm\(^{-3}\) was LT (10\(^{-1}\), 30, 10\(^3\)) cm\(^3\) g\(^{-1}\) and that for 0.1 mol dm\(^{-3}\) being (10\(^{-2}\), 5, 200) cm\(^3\) g\(^{-1}\) [A7] with lower, best estimate and upper bounds being supported by available experimental data [A7].

The approach used to integrate the impact cement aging into PDFs for radioelement sorption [A3] was applied to ISA sorption onto cement. This involved the conversion of log triangular PDFs into standard seven-point PDFs used for radioelement sorption [A3, A7]. ISA sorption was then adjusted to take into account cement aging by applying the following:

\[
K_d^\ast(p) = \frac{K_d(p)}{10^\Delta F(p)} \tag{A1.1}
\]
Where $K_d(p)$ is the sorption of ISA onto pristine cement at probability value $p$, $K_d^*(p)$ is the sorption of ISA onto aged cement at probability value $p$, $AF(p)$ is an aging factor dependent on $p$. Revised PDFs resulting from the application of the above equation can be found in Table 4 (main text), this data was also used to generate ISA sorption data for situations where the initial ISA concentration is not known [A7].

In order to convert SEFs and SRFs from being a function of cellulose loading to being a function of the pore water CDP concentration a mathematical treatment was developed [A7]. This assumed that CDPs could be represented by a single dissolved compound X which has a molecular weight $M_x$. By reference to experimental data [A9, A10] on CDPs a value of 160 g mol$^{-1}$ was chosen for $M_x$. This mathematical treatment is outlined below, for a full derivation of this treatment readers are referred to Chambers and Williams [A7].

$$C_x^* = F \frac{FC}{[M_x(W + K_d)]} \quad (A1.2)$$

Where $C_x^*$ is the aqueous concentration of compound X taking into account that a fraction of X has sorbed onto the cement, $F$ is the conversion factor between cellulose and CDP which takes into account the water consumed on cellulose degradation, $C$ is the cellulose loading, $W$ is the water to solid ratio and $K_d$ is the sorption distribution coefficient of compound X. An example application of this approach can be found in Chambers and Williams [A7].

As with near-field research [A11] the investigation of sorption of CDPs onto geosphere materials has focussed on ISA. Data on tuff from the UK demonstrated significant ISA sorption at low initial ISA concentrations [A8] (Table A2) indicating that geosphere ISA concentration would be reduced by this process with an associated reduction in radioelement complexation and mobility [A1]. Geosphere sorption of ISA is host rock specific. Experiments involving calcite found negligible ISA sorption [A12] whereas experiments involving Boom clays only found statistically significant sorption at ISA concentrations lower than 0.3 mM [A13].

To further investigate the impact of organic complexants on radioelement migration a story board approach [A14] has been developed to provide a systematic method for prioritising area where data is absent and an understanding of the processes involved is lacking. This approach summarised variations in the chemical and physical parameters through the various regions considered in performance assessment at four timeframes (Table A3). Stability and availability factors were applied to the organic complexants under consideration. The stability factor (SF) refers to the stability of the organic compound to degradation and the availability factor (AF) includes transport and accessibility considerations as well as dilution, precipitation and sorption. These two factors were then combined to give an overall weighting factor (WF) for each complexant in each region and timeframe. WF values of ≥7 were considered most significant. In terms of CDP this study employed the term Authentic Cellulose Degradation Products (ACDP) and split this into ISA-like components and gluconate and non-ISA like components (e.g. organic acids). In addition ISA was considered on its own. WF for ISA suggested that it is likely to be most significant in near-field and alkaline disturbed zone. Beyond this zone the WF for ISA decreases based on the assumption that microbial activity will remove ISA as it enters the host rock. However, the authors [A14] recognise that further evidence was required to demonstrate that ISA can be degraded in the geosphere. If this was shown not to be the case, it was recognised that ISA complexation could significantly impact the migration of some radioelements. It was recognised however, that dilution and dispersion processes in the geosphere would reduce the overall impact of ISA complexation from a radionuclide migration perspective.

A1.4 References


A12. J. Tits, E. Weiland and M. H. Bradbury, *The Effect of Isosaccharinic Acid and Gluconic Acid on the Retention of Eu(III), Am (III) and Th(IV) by Calcite*, Applied Geochemistry 20, 2082-2096, 2005.


Table A1. Assumptions, influencing factors and sources of uncertainty and relevant to the elicitation of ISA sorption PDFs [A7]

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Relevant Factors</th>
<th>Sources of Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>• pH is in the range of pH 10 to 13.</td>
<td>• Pore water pH.</td>
<td>• Chemical nature of the cement.</td>
</tr>
<tr>
<td>• Temperature in the range of 15°C to 80°C.</td>
<td>• Porosity.</td>
<td>• Ionic strength of the pore water.</td>
</tr>
<tr>
<td>• Materials are homogeneously distributed.</td>
<td>• Competition for sorption site between ISA and other anions.</td>
<td>• Water to solid ratio.</td>
</tr>
<tr>
<td>• All processes have achieved thermodynamic equilibrium.</td>
<td>• Pore water ionic strength.</td>
<td></td>
</tr>
<tr>
<td>• Pore water ionic strength is in the range of 0.1 to 1.5 mol dm$^3$.</td>
<td>• Surface charge properties of the cement.</td>
<td></td>
</tr>
<tr>
<td>• Competition and site saturation effects will be important.</td>
<td>• Temperature.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Effect of complexation of ISA with dissolved metal ions.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Type of cement.</td>
<td></td>
</tr>
</tbody>
</table>
Table A2. ISA sorption onto Sellafield tuff [A8]

<table>
<thead>
<tr>
<th>Initial ISA concentration (mol dm$^{-3}$)</th>
<th>Sorption Distribution Ratio, Rd, (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{-3}$</td>
<td>2</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>3</td>
</tr>
<tr>
<td>$2 \times 10^{-5}$</td>
<td>13</td>
</tr>
<tr>
<td>$2 \times 10^{-6}$</td>
<td>10</td>
</tr>
<tr>
<td>$2 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$2 \times 10^{-8}$</td>
<td>26</td>
</tr>
<tr>
<td>$2 \times 10^{-9}$</td>
<td>14</td>
</tr>
</tbody>
</table>

* Experiment conducted in the presence of approximately $2 \times 10^{-7}$ mol dm$^{-3}$ uranium(VI) and approximately $6 \times 10^{-11}$ mol dm$^{-3}$ plutonium

Table A3. Storyboard timescales and regions [A14]

<table>
<thead>
<tr>
<th>Time Frame</th>
<th>Period (Years)</th>
<th>Region most mobile species are assumed to have reached</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10s to 100s</td>
<td>Disturbed Zone</td>
</tr>
<tr>
<td>2</td>
<td>100s to 1,000s</td>
<td>Host Rock/Reducing Layer</td>
</tr>
<tr>
<td>3</td>
<td>10,000s</td>
<td>Oxidising layer/Near-surface</td>
</tr>
<tr>
<td>4</td>
<td>100,000</td>
<td>Biosphere</td>
</tr>
</tbody>
</table>