ER-0791 Degradation of cellulose under disposal conditions

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Nele Bleyen

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Degradation of cellulose under disposal conditions
State-of-the-art report

Authors: Nele Bleyen
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<td>CDP</td>
<td>cellulose degradation product</td>
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<td>CI</td>
<td>crystallinity index</td>
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<td>DOC</td>
<td>dissolved organic carbon compounds</td>
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<td>DP</td>
<td>degree of polymerisation</td>
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<td>IR</td>
<td>infrared spectroscopy</td>
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<td>ISA</td>
<td>isosaccharinic acid</td>
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<td>MSA</td>
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Preface

This state-of-the-art report contains a literature survey regarding cellulose degradation processes in conditions relevant to the disposal of cellulose-containing radioactive waste. The survey was performed within the study 'RS 18_SCK_BIT_08: State-of-the-art report on cellulose degradation' of the research package RP BIT (contract number CO-90-14-3690-00 / CCHO 2015-0304/00/00).
Abstract

Cellulosic materials are present in significant amounts in Belgian nuclear waste, which is currently envisaged to be disposed of in a surface (low- or intermediate-level short-lived waste) or deep geological repository (intermediate-level long-lived waste) by ONDRAF/NIRAS, the Belgian radioactive waste management organisation. The massive employment of cementitious structural and backfill materials will result in the generation and long-term persistence of a high pH (pH > 12.5) environment within the disposal system. Cellulose is susceptible to both alkaline and radiolytic degradation, which result in the formation of cellulose degradation products. Under highly alkaline conditions, some of these cellulose degradation products (e.g., α-isosaccharinic acid) are able to complex strongly with multivalent radionuclides, thereby possibly enhancing the transport of these radioactive species to the biosphere. This report reviews the current understanding regarding alkaline and radiolytic cellulose degradation processes and the associated kinetics and degradation products. Also the stability of certain degradation products under radioactive waste disposal conditions is addressed briefly.

Keywords

Cellulose, radioactive waste, alkaline degradation, radiolytic degradation
1 Introduction

Cellulosic materials are expected to be present in a significant amount of Belgian nuclear waste, which is proposed for disposal in either a surface facility (for low- or intermediate-level short-lived waste) or in a deep geological disposal facility (for intermediate-level long-lived waste). Indeed, the widespread use of this polymer in the nuclear industry (i.e. as paper, tissues, filters, wood and textiles) has resulted in cellulose-based materials making up large quantities of certain (mostly older) waste streams. An important reason for this is that in the past up to 10 kilograms (and in exceptional cases even more) of cellulose-based materials were allowed in one 400 liter drum. It is estimated for the near surface disposal facility that thousands of 400 liter conditioned waste drums contain several kilograms of cellulose-based material. For the geological disposal facility a significant amount of 400 liter drums will contain more than 10 kilogram of cellulose-based materials. The quantities of cellulose that are allowed in the nuclear waste are being (severely) reduced, since it is acknowledged that degradation of cellulose can lead to the release of complexing agents. Co-disposal of high quantities of cellulose with radionuclides can therefore increase migration of radionuclides from the disposal facility into the biosphere.

Under the anoxic and alkaline conditions imposed by the excess of cementitious materials in such facilities (see Section 3.2) and/or in the presence of radiation, cellulose is susceptible to degradation processes, which result in the formation of soluble cellulose degradation products (CDPs). Under the highly alkaline conditions prevailing in the disposal facility, some of these organic compounds, such as isosaccharinic acid (ISA), could form strong complexes with multivalent radionuclides (RN), which could enhance the transport of the RN present in the waste. Understanding the reaction mechanisms and kinetics of cellulose degradation is therefore of high interest for safety assessment calculations for the disposal facilities of radioactive waste.

In this report, the current knowledge regarding cellulose degradation under radioactive waste repository conditions will be discussed:

- Chapter 2 describes the chemical and physical structure of cellulose, including the supramolecular and different morphological structures;
- The presence of cellulose in certain nuclear waste packages and the concept of their disposal is discussed in Chapter 3;
- Chapter 4 describes the mechanisms, the kinetics and the products of cellulose degradation and focusses on alkaline and radiolytic degradation of cellulose;
- Finally, the chemical stability of one of the most important degradation products, isosaccharinic acid, is discussed in Chapter 5.
2 Cellulose: chemical composition and structure

2.1 Molecular structure

Cellulose is a structural polysaccharide found as the major component of cell walls in plants and certain bacteria, fungi, algae and marine animals, with its primary natural function being the protection of cells and the provision of structure and support (Zubay 1998; Iguchi et al. 2000; Kimura et al. 2001; Ioelovich 2016). Polysaccharides are high molecular weight carbohydrates, composed of simple or derived sugars connected by glycosidic bonds. Cellulose chains are unbranched linear homopolymers of β(1,4)-linked D-glucopyranose monomeric units, with each unit being in the chair configuration (Figure 1) (Nehls et al. 1994; Klemm et al. 1998; Zubay 1998).

The number of incorporated glucose units per cellulose chain is referred to as the degree of polymerisation or DP. Commonly, the DP of cellulose can be determined after dissolution of the cellulose in a suitable solvent using a viscometer or using size exclusion chromatography (Shibazaki et al. 1995; Klemm et al. 1998; Van Loon et al. 1999a; Hallac and Ragauskas 2011). Both techniques provide an accurate average value of the degree of polymerisation, though the obtained values can differ slightly for one source of cellulose depending on the solvent used and the temperature (Hallac and Ragauskas 2011). When a viscometer is used, the DP is defined as the viscosity average DP (DP_v) or the weight average (DP_w) degree of polymerisation, as defined in equations 1 to 3:

\[ DP_v = \frac{M_v}{MW_{glucose}} \text{ with } M_v = \frac{\sum N_i \eta}{\sum N_i} \text{ and } \eta = K_m M^{\alpha+1} \]  
Equation 1

\[ DP_n = \frac{M_n}{MW_{glucose}} \text{ with } M_n = \frac{\sum N_i M_i}{\sum N_i} \]  
Equation 2

\[ DP_w = \frac{M_w}{MW_{glucose}} \text{ with } M_w = \sum \left( \frac{N_i M_i M_j}{\sum N_i M_i} \right) \]  
Equation 3

where \( M_v \) is the viscosimetry average molecular weight, \( MW_{glucose} \) is the molecular weight of anhydroglucose (162 g mol\(^{-1}\)), \( N_i \) is the number of moles of a given cellulose fraction \( i \) having molar mass \( M_i \), \( \eta \) is the intrinsic viscosity, \( K_m \) and \( \alpha \) are experimentally derived constants (with \( \alpha \) ranging from 0.75 - 1 for cellulose and its derivatives), \( M_v \) is the number average molecular weight and \( M_w \) is the weight average molecular weight (Hallac and Ragauskas 2011).

The DP of cellulose can vary strongly depending on the origin and/or the industrial treatment applied to it. Typical DPs range from several hundreds (for industrially processed cellulose) to over ten thousands for e.g. wood (Updegraff 1969; Ioelovich 2016). Industrial treatment of cellulose decreases the DP significantly. For instance, the DP of cotton cellulose decreases from ~2100 (untreated cotton) to 1500 (after isolation and bleaching of cellulose), down to several hundreds after acid hydrolysis during industrial processing (Updegraff 1969; Topalovic et al. 2007; Ioelovich 2016). Cellulose chain length can affect the mechanical properties of the cellulosic materials and its solubility in certain solvents (Heinze and Koschella 2005; Zhuravleva et al. 2017).

A cellulose chain has a non-reducing and a reducing end group. The non-reducing end is the terminal glucose unit, which is a closed ring structure. The reducing end group is a free monomeric unit that is only on one side involved in a glycosidic bond. Due to this, the reducing end monomeric unit is able to convert into its open-chain form, i.e. this unit consists of a cyclic hemiacetal in equilibrium with a reducing aldehyde group (Figure 1; Kontturi et al. 2006; Calvimontes et al. 2011).
2.2 Supramolecular structure

During biosynthesis of cellulose, cellulose chains are arranged in a well-defined supramolecular structure. Along the cellulose chain, the free hydroxyl groups and hydrogen atoms are positioned equatorially and axially respectively (Figure 1). The functional groups from one chain form hydrogen bonds with the oxygen atoms (both the ring and bridging oxygen atoms) on the same or on a neighbouring chain, resulting in a high affinity of the polymer chains for one another. This way, many individual cellulose chains assemble together to form elementary fibrils or nanofibrils. Aggregation of these nanofibrils by coalescence results in the formation of microfibrils (diameter < 0.035 µm). This aggregation phenomenon is supported by van der Waals forces, as well as intra- and intermolecular hydrogen bonds. Coated on the microfibrils of native cellulose is hemicellulose1, present as a supportive matrix, effectively tethering the microfibrils to one another. Many microfibrils arranged in parallel comprise a macrofibril (diameter < 1 µm) and several of these combine into a cellulose fibre, with a diameter between 10 and 50 µm (Zubay 1998; Gomez et al. 2008; Chinga-Carrasco 2011). Note that pretreatment of cellulosic material during e.g. paper making results in the removal of (part of) the hemicellulose.

Cellulose microfibrils contain distinct domains with variable levels of cellulose chain ordering: i.e. the cellulose microfibrils have regions of low order (amorphous) and regions of high order (crystalline). In addition, recent experimental data on the mechanical, chemical and physicochemical properties of cellulose suggest the existence of intermediately ordered regions (paracrystalline), which are crystalline though disordered (without regular packing of the cellulose chains) (Nishiyama et al. 2003a; Inagaki et al. 2010; Moon et al. 2011; Kulasinski et al. 2014; Martinez-Sanz et al. 2017). The three levels of cellulose chain ordering are represented in Figure 2.

Figure 2: Atomistic simulation of the different states of cellulose Iβ: (a) crystalline; (b) paracrystalline and (c) amorphous (Kulasinski et al. 2014).

Recently, a new model of the arrangement of these different domains within a cellulose microfibril has been proposed, based on the generally accepted model though taking into account the existence of paracrystalline regions. In this model, each microfibril is built from ordered crystallites and less ordered amorphous domains, alternating along the fibril, but also covered by a thin layer of paracrystalline cellulose chains as represented in Figure 3 (Ioelovich et al. 2010; Kulasinski et al. 2014; Ioelovich 2016; Martinez-Sanz et al. 2017). This model seems to be able to forecast the various properties of cellulose adequately, including the decrease in DP due to hydrolysis and the formation of nanoscale crystalline cellulose after acid hydrolysis2, which previous models failed to predict (Ioelovich 2016).

---

1 Hemicelluloses are naturally occurring branched, short chain polysaccharides, i.e. modified xylans, galactoglucomannans, glucomannans and arabinogalactans.
2 Acid hydrolysis of cellulose is an important process used in the production of ethanol from biomass, but also produces cellulose micro and nano crystals are being produced as end product. In this process, cellulose is partially degraded, thereby removing (part of) the amorphous and paracrystalline regions, while leaving the crystalline parts unaffected (Palme et al. 2016).
The relative amount of highly ordered, crystalline material within cellulose is represented as the crystallinity index (CI) and is depending on the origin and treatment of the cellulose. This degree of crystallinity affects the physical and chemical properties of the polymer; e.g., tensile strength, dimensional stability and density increase with increasing CI, while flexibility, swelling and chemical reactivity decrease with increasing CI (Fukuzumi et al. 2009; Agarwal et al. 2010). According to Müller et al. (1998) and Nishiyama et al. (2003a), hydroxyl groups of the disordered regions are indeed more accessible than those of crystalline regions, which explains the enhanced chemical reactivity with decreasing CI. Chemical degradation (under acid or alkaline conditions) of cellulose therefore takes place in the disordered regions of cellulose rather than in the crystalline regions. Cellulose with a low CI therefore tends to degrade at a higher rate compared to cellulose with a high CI.

Note that paracrystalline cellulose is believed to be a non-equilibrium state between the crystalline and amorphous cellulose states. Under certain conditions (e.g., submerging cellulose in hot and/or compressed water), a conversion of crystalline regions into amorphous regions has been observed, presumably via their paracrystalline state. Such transformation is believed to be due to cleavage of certain inter- and/or intramolecular bonds (Sasaki et al. 2000; Degushi et al. 2008; Kulasinski et al. 2014).

### 2.3 Morphological structure of crystalline cellulose

The unbranched cellulose chains and the ability to form hydrogen bonds enable the polymer to crystallise in several ways. At this moment, there are six known interconvertible allomorphs of crystalline cellulose, i.e. cellulose I, II, III, IV, and IV (Figure 4), although there is debate regarding the existence of cellulose IV. These six allomorphs are distinguishable based on the way that the individual cellulose polymers are hydrogen-bonded together, resulting in differences in unit cell dimensions and chain polarity (Hayashi et al. 1975; Kolpak and Blackwell 1976; Zubay 1998; Gross and Chu 2010). Both cellulose I and IV have been found in several natural primary cell walls, while cellulose II and III can only be produced artificially (Klemm et al. 1998). As the morphological structure can affect the overall chemical degradation rate of cellulose (see Section 4.1.2.1), more details regarding the six allomorphs are shown in the next sections.

![Figure 4: Interconversion of the allomorphs of cellulose.](image-url)
2.3.1 Cellulose I

Native cellulose crystallises as cellulose I, which consists of parallel chains (with respect to its direction from non-reducing to reducing end) held together by intrachain hydrogen bonds between adjacent monomeric units and by an interchain bond between neighbouring chains, thereby forming one sheet (Figure 5A). No hydrogen bonds occur between chains of different sheets. Instead the sheets are held together with van der Waals bonds (Zubay 1998; Gross and Chu 2010).

![Figure 5: Hydrogen bond network (indicated in green) in (A) cellulose I and (B) cellulose II. Note also the parallel vs anti-parallel arrangement of the individual chains of cellulose I and II respectively (adapted from Kontturi et al. (2006)).](image)

Based on nuclear magnetic resonance (NMR), infrared spectroscopy (IR), crystallographic and electron diffraction analysis, cellulose I is actually a composite of two crystalline forms, Iα and Iβ. These two forms are assigned to the triclinic and the monoclinic crystal structure respectively (Atalla and Vanderhart 1984; Horii et al. 1987; Sugiyama et al. 1991; Nishiyama et al. 2002; Nishiyama et al. 2003b; Popescu et al. 2011). The triclinic structure is metastable and can be converted to the stable monoclinic form upon hydrothermal annealing treatment (Sugiyama et al. 1991). Depending on its origin, native cellulose contains different alpha to beta content ratios (Wada et al. 1993, 1995, 2001). The metastable Iα is typical for cellulose of algae and bacteria, while the stable Iβ dominates in the cellulose of plants and animals (O’Sullivan 1997; Ioelovich 2016).

2.3.2 Cellulose II

Cellulose II is the crystalline form that emerges by regeneration (i.e. re-crystallisation after solubilisation) or by mercerisation, i.e. after swelling of native cellulose in concentrated sodium hydroxide and removal of the swelling agent. During the first step of mercerisation, the NaOH molecules separate the microfibrils by entering the polymer structure, thereby forming so-called Na-cellulose complexes. This process results in an immediate transition in the crystal structure and in the chain packing of the microfibrils. It ultimately leads to swollen cellulose fibres (or regions within each fibre) and opening up of the polymer structure. After removal of the swelling agent, the linked Na-ions will be removed and the Na-cellulose will transform into the cellulose II structure (Crawshaw et al. 2002; Hashim et al. 2012). This polymorph is thermodynamically the most stable crystalline form of cellulose and the conversion of cellulose I into cellulose II is therefore irreversible (Klemm et al. 1998). The silk-like texture of cellulose II materials means that they are widely applied in the textile industry, though it also has other applications, such as its use in transparent films and filters (Moon et al. 2011).

Like cellulose Iβ, cellulose II has a monoclinic crystal structure (Kolpak and Blackwell 1976). In contrast to cellulose I, cellulose II has an anti-parallel chain packing and a different hydrogen bond network, i.e. though the dominant intra-chain hydrogen is the same for both polymorphs, the inter-chain hydrogen bonds are different (Figure 5B) (Kolpak and Blackwell 1976; Fengel et al. 1995; Raymond et al. 1995; Langan et al. 1999; Langan et al. 2001; Nishiyama et al. 2002; Nishiyama et al. 2003b; Kontturi et al. 2006). Furthermore, also inter-sheet hydrogen bonding occurs in cellulose II, resulting in its higher mechanical stability compared to cellulose I (Kolpak and Blackwell 1976).
2.3.3 Cellulose III and IV

The remaining polymorphs of cellulose are III and IV, and will only be very briefly discussed, as these polymorphs are believed to be less present in nuclear waste. These allomorphs can be classified further into I and II (Figure 4), depending on whether their unit cell and polarity is similar to that of cellulose I and II, which are their respective precursors.

Treating cellulose I or II with anhydrous liquid ammonia or diamine and evaporation of excess ammonia gas will reversibly form cellulose III, and III' respectively. Liquid ammonia or amine treatment is believed to cause swelling of the cellulose structure and the ammonia or amine will penetrate its crystal structure to yield a cellulose-ammonia complex. The interaction between cellulose and the ammonia or amines causes changes in the interplanar distances, resulting in larger crystal unit cells, which will only partially decrease upon evaporation of the ammonia or amines. The result of this treatment is the cellulose III allomorph. Due to the larger crystal unit cells, it has been suggested that cellulose III has an enhanced chemical reactivity compared to native cellulose. Both cellulose III, and III' can be converted back to their starting material by (hydro)thermal treatment. The detailed structural differences between cellulose III, and III' have however not been established yet (Wada et al. 2004a; Mittal et al. 2011).

Cellulose IV, and IV' can be prepared from the corresponding form of cellulose III, and III' by heating in glycerol (at 260 °C). However, recent evidence from X-ray diffraction, IR or NMR analyses and diffraction simulation studies suggests that cellulose IV could be a slightly disordered form of cellulose Iβ (Wada et al. 2004b; Newman 2008; Nishiyama 2009).

2.4 Substitution of cellulose

Cellulose derivatives can be made by substituting one of the hydroxyl groups with an aromatic, methyl, ester or ether group. Such cellulose derivatives are applied in diverse areas, such as laminates, optical films, textiles and coatings for pharmaceuticals and foods. The substitution of the cellulose monomers with such a new functional group ensures that crosslinking of the polymers is possible (under the right conditions), which changes its properties (gel versus solid state) and its applications (Klemm et al. 2005).

2.5 Porosity and internal surface area

In addition to the fibrillar structure of cellulose fibres, they contain a pore network and inner voids, with an average pore size and porosity depending on the origin of the cellulose and their crystallinity and morphological structure (Klemm et al. 1998). Average pore sizes tend to range from a few nm to 25 nm wide. Two to six times higher internal surface areas (based on water vapor sorption) are observed for native or amorphous cellulose compared to microcrystalline cellulose3, indicating that crystalline cellulose has a lower porosity and/or smaller pore sizes compared to amorphous cellulose (Tantasucharit 1995; Klemm et al. 1998; Ioelovich 2009). The accessibility of the inner regions of cellulose to water or other reagents such as NaOH is linearly related to the internal surface area and is therefore inversely related to the crystallinity degree of cellulose. Nevertheless, although the internal surface area of pure crystalline cellulose is often considered to be zero, this has not been confirmed experimentally (Ioelovich 2009).

Furthermore, treatment of the fibres will generally result in alteration of the total pore volume and pore size distribution. For instance, mercerisation of cellulose I and thus formation of cellulose II ultimately leads to an enhancement of internal surface area. In general, interfibrillar and intercrystalline swelling of cellulose fibres in aqueous solutions tend to increase the pore volume due to water uptake. Although re-drying of these swollen cellulose fibres causes a reduction of the pore volume (compared to the swollen state) due to collapse of the (smallest) pores by the high capillary forces and further formation of hydrogen bonds block the collapsed pore and prevent its re-opening, the total accessible internal surface area in mercerised cellulose is higher than in the native form (Ishikawa and Okano 1997; Klemm et al. 1998).

Due to the pore network and the voids, the total surface area of cellulose fibres exceeds by far the geometrical outer surface. The accessible inner surface area is an important factor playing a decisive role with regard to chemical reactivity (Fink et al. 1992; Klemm et al. 1998).

3 Microcrystalline cellulose is produced by partially depolymerising cellulose (DP < 400), during which the disordered regions are partially removed, while leaving the crystalline regions intact. This process results in smaller cellulose chains and in a higher overall crystallinity (compared to the original cellulose).
3 Cellulose in radioactive waste

3.1 Origin

Cellulose is one of the most abundant organic materials on earth, used in the production of paper, as one of the main ingredient of textiles (for textile made from cotton, linen, etc), in the pharmaceutical and food industry (as microcrystalline cellulose) and many others. Also in the nuclear industry cellulosic materials have been commonly used, which end up in the radioactive waste, and form a substantial part of the organic waste: paper, tissue, filters, cloth and wood. The latter materials consist partially of cellulose, commonly as allomorphs I or II and/or cellulose derivatives (see Sections 2.3 and 2.4).

3.2 Disposal of cellulose-containing radioactive waste

The Belgian radioactive waste management organisation, ONDRAF/NIRAS, is responsible for the long-term management and final disposal of radioactive waste. For this management, ONDRAF/NIRAS has adopted a hierarchical classification scheme for conditioned radioactive waste, which takes into account the activity level and half-life of the radionuclides contained in the waste at the time of conditioning (in accordance with international recommendations (EU 1997)), as well as the heat generated by the waste due to radioactive decay (Smith et al. 2009; ONDRAF/NIRAS 2010):

- Category A waste is short-lived low-level and intermediate-level conditioned waste that contains trace quantities of long-lived radionuclides.
- Category B waste is low-level and intermediate-level conditioned waste containing long-lived radionuclides in such quantities that it presents a risk over time periods ranging from several tens to several hundreds of millennia for some of the waste. Its thermal power is potentially significant at conditioning, but it emits too little heat after its storage period to be classified as category C waste.
- Category C waste is high-level conditioned waste containing large quantities of long-lived radionuclides and which, like category B waste, therefore presents a risk over time periods ranging from several tens to several hundreds of millennia for some of the waste. Its thermal power will lead to a significant rising of the temperature of its environment during long-term disposal.

Cellulosic wastes, including paper, tissue, filters, cloth and wood, form a significant proportion of the organic materials in category A and B waste packages. All of these cellulose-containing waste is embedded in a cement matrix. The vision of ONDRAF/NIRAS for the long-term disposal of both waste categories is discussed in the next sections 3.2.1 and 3.2.2.

3.2.1 Surface disposal of category A waste

For category A waste, the steepest decline of radioactivity, and therefore of radiological hazard occurs within the first hundreds of years after emplacement of the waste. Beyond some thousands of years the radiological hazard reaches a residual level due to the trace amounts of long-lived radioactivity (ONDRAF/NIRAS 2010; Van Geet et al. 2012; ONDRAF/NIRAS 2019c).

The disposal system of category A waste is a surface disposal facility, composed of structurally independent concrete modules, in which the waste packages will be encapsulated using mortar in concrete monoliths. The modules are placed on a sand-cement embankment (Figure 6). After waste emplacement, the modules are overlain by a multi-layer cover (including a steel roof, concrete and earth layers) to form a mound to prevent water intrusion for at least 1000 years. Water is diverted away from the inside of the module either by the steel roof, by the clay barrier in the earth cover and/or by the impervious concrete top slab. (ONDRAF/NIRAS 2010; Van Geet et al. 2012; ONDRAF/NIRAS 2019c).

Because of the very low water flux in the system during the first 1000 years, the inside of the module will re-saturate only slowly, while the voids and intermonolith spaces will remain unsaturated. Furthermore, the limited water infiltration will result in anoxic conditions in the entire repository as the low amount of oxygen entering the system will be consumed rapidly by corrosion or other O₂-consuming processes. The low water flux will also lead to a depletion of CO₂ and thus in a limited cement degradation in the modules and monoliths. The pH of the cement pore water inside the monoliths is therefore expected to be higher or near 12.5 (depending on the location and the conditioning matrix of the waste) (ONDRAF/NIRAS 2019c).
After the first 1000 years, the physical integrity of the top cover and/or the module walls can no longer be guaranteed. It is expected that either the module walls (and subsequently the inside of the modules) and/or the impervious top slab will gradually degrade and a fracture network will be formed. Water will flow in the unsaturated spaces between the monoliths and with time also in the monolith itself (through fractures) and in the module basis. The redox conditions will gradually evolve towards more oxic conditions and thus less reducing conditions due to infiltration of oxygen-rich water. It can however be assumed that reducing and oxidising conditions will co-exist depending on the location in the disposal facility, at least initially. Most probably, reducing and anoxic conditions can still be expected inside the waste packages, at least for as long as the monoliths maintain their physical integrity. The pH in the repository will evolve strongly once water flows through the modules, though inside the waste, the pH is expected to remain near or above 12.5 for as long as limited advective water flow occurs inside the monolith (ONDRAF/NIRAS 2019c).

![Cross-sectional view of the near surface disposal facility for category A waste](image)

**Figure 6:** Cross-sectional view of the near surface disposal facility for category A waste (adapted from ONDRAF/NIRAS, 2019a).

### 3.2.2 Deep geological disposal of category B waste

Category B waste contains long-lived radionuclides in such quantities that it presents a risk over time periods ranging from several tens to several hundreds of millenia.

The reference disposal concept of category B waste entails the immobilisation of the category B waste drums in mortar inside monoliths. Several designs of such monoliths exist to accommodate the large variety of primary waste packages (Figure 7). One monolith may contain waste packages from different families, to manage the variability of their characteristics. These monoliths will then be placed in concrete-lined, horizontal geological disposal galleries, excavated at nearly mid-depth in the host formation, for which currently a plastic clay is envisaged (Figure 7). All voids inside the monoliths (except for inside the drums) and between the monoliths and the gallery liner will be backfilled with cement-based materials. The overlying sedimentary formations will provide the geological barrier to isolate the waste and delay the migration of radionuclides towards the biosphere in time. After closure of the disposal gallery, pore water will gradually fill the disposal facility, which is expected to be saturated after ~50 to 100 years. Due to the high amount of cement-based materials present in the disposal facility, an alkaline environment is expected with a pH equal to or higher than 12.5 for long periods of time. Furthermore, the oxygen in the disposal facility will rapidly disappear due to radio-oxidation, aerobic corrosion, diffusion into the environment and, if present, microbial activity. Afterwards, reducing conditions are expected inside the disposal facility (Weetjens et al. 2006; Wang et al. 2010; ONDRAF/NIRAS 2013).
Figure 7: (a) Reference concept for geological disposal of category B and C waste, consisting of a network of horizontal disposal galleries inside a host formation (artistic view); (b) Two designs of monoliths for category B waste (left: 200 L drums and right: compacted waste) (ONDRAF/NIRAS 2013).
4 Cellulose degradation under disposal conditions

As cellulose can be found both in category A and B waste packages, both disposal concepts should be taken into account when assessing its degradation under disposal conditions. However, in both cases, a highly alkaline pH (originally expected to be 13.5 but dropping to 12.5 as the cementitious materials mature and evolve (Jacques et al. 2010; Wang et al. 2010)) and a reducing / anoxic environment is expected, at least inside the waste drums, for a relatively long period of time (relatively in regard to the radiological hazard; see Section 3.2). Degradation of cellulose should therefore be assessed under these conditions, and can occur either through chemical reactions or radiolytic processes. Chemical degradation of cellulose under alkaline conditions will result in the production of RN-complexing organic cellulose degradation products (CDPs), in particular isosaccharinic acid or ISA. On the other hand, irradiation of cellulose leads predominantly to chain scission and thus smaller cellulose chains. Both degradation processes will be discussed in the next sections.

Note that cellulose can also be degraded by microbes performing enzymatic hydrolysis of cellulose and oxidation of CDPs, such as ISA. Microbial cellulose degradation would ultimately result in the production of acetate and would in turn lead to local acidification and a marked decrease in alkaline cellulose degradation rate (Bassil et al. 2015a). Additional microbial ISA degradation would further decrease the amount of such complexing agents leaching from cellulose-containing radioactive waste (Bassil et al. 2015b). Nevertheless, as microbial growth and activity at such high pH and in the presence of radiation cannot be guaranteed, it is difficult to ensure that these reactions will indeed take place at a significant rate inside the repository. At this moment, a conservative approach is therefore followed when performing performance assessment calculations for the disposal of cellulose-containing radioactive waste, which does not include a possible microbial cellulose and ISA degradation. Microbial cellulose degradation is therefore not discussed in detail in this report.

4.1 Chemical degradation at highly alkaline pH and anoxic conditions

Under alkaline and anoxic conditions, cellulose is known to be rather unstable and to degrade into water soluble CDPs. The two major CDPs are α-isosaccharinic acid (3-deoxy-2-C-(hydroxymethyl)-erythro-pentonic acid) and β-isosaccharinic acid (3-deoxy-2-C-(hydroxymethyl)-threo-pentonic acid) (Whistler and BeMiller 1958; Greenfield et al. 1994a and b; Van Loon and Glaus 1998; Knill and Kennedy 2003), of which the structure is shown in Figure 8. In addition, a large number of small chain fatty acids and glucose derivatives are formed during anoxic, alkaline degradation of cellulose, though each in smaller amounts (Van Loon and Glaus 1998; Glaus et al. 1999).

The following distinct reaction pathways have been identified, which contribute to the alkaline degradation of cellulose:

- Peeling reaction
- Stopping reaction
- Mid-chain scission

All three pathways can occur, but compete with each other. In the next sections, these reaction mechanisms will be discussed more in detail.
4.1.1 Reaction mechanisms

4.1.1.1 Peeling or end-wise degradation reaction

In general, alkaline degradation of polysaccharides begins at the reducing end of the molecule and proceeds in a stepwise manner along the polymer chain. Each reaction removes an individual glucose unit from the reducing end of the cellulose chain and generates a new reducing end, allowing the reaction to continue (Figure 9).

The peeling reaction is initiated by an alkaline-induced aldose-to-ketose isomerisation, resulting in the activation of the reducing end group. Afterwards, a β-alkoxycarbonyl elimination reaction takes place, which removes the end group from the remainder of the cellulose chain. Finally, benzilic acid type rearrangement commonly occurs, which produces α- and β-ISA. Nevertheless, depending on the nature of the cations present (see Section 4.1.2.3), fragmentation of the 4-deoxy-2,3-hexodilulose can occur as well, which leads to the production of a number of other smaller organic acids (e.g. formic and lactic acid) (Machell and Richards 1958; Speck 1958; Whistler and BeMiller 1958; Machell and Richards 1960b; Sjöström 1977; Ziderman and Belayche 1978).
Figure 9: Simplified overview for the chemical degradation reactions for cellulose under alkaline conditions. Details regarding the ongoing reactions can be found in Section 4.1.1. Glucose monomeric units; reducing end group; activated reducing end group (by aldose to ketose isomerisation); intermediate product (4-deoxy-2,3-hexodilulose) formed after peeling off a glucose monomer from the cellulose chain; metasaccharinic acid (MSA) end group, which stops the peeling reaction from continuing.
4.1.1.2 Stopping reaction

If the peeling reaction would be the only reaction taking place, cellulose would be completely dissolved in an alkaline solution. However this is not the case, since this reaction competes with 2 stopping reactions, i.e. a chemical and a physical stopping process.

The chemical stopping reaction terminates the end-wise degradation by forming alkali-stable end groups (Figure 9) and thereby stabilizes the cellulose chain in an alkaline environment (Machell and Richards 1960b). In this stopping reaction, the activated reducing end group is converted to a nonreactive metasaccharinic acid (MSA) end group, through a combination of a β-hydroxycarbonyl elimination and benzilic acid type rearrangement of the intermediate product (Figure 9) (Machell and Richards 1960b; Haas et al. 1967).

In addition, the physical stopping occurs when the end-wise degradation reaction reaches an inaccessible, crystalline region of the cellulose microfibrils (Machell and Richards 1958; Haas et al. 1967; Gentile et al. 1987; see also Section 2.5). Since the transition from the amorphous to the crystalline region is considered not to be a distinct interface, the physical stopping reaction will not occur abruptly, but rather gradually within the cellulose microfibrils (Gentile et al. 1987). When physical stopping occurs, the degrading chains terminate with a normal reducing end group at the crystalline-amorphous transition region (Gentile et al. 1987).

As both the peeling and the stopping reactions are competing reactions, the extent and rate of cellulose degradation is depending on the ratio between both reaction rates (see Section 4.1.3).

4.1.1.3 Alkaline hydrolysis or mid-chain scission reaction

At high temperatures (> 140 °C), alkaline hydrolysis of cellulose has also been observed. This degradation mechanism causes random chain scission, i.e. cleavage of the glycosidic bonds (Figure 9), either between the oxygen atom and the glycosyl group or between the oxygen atom and the aglycone4 group. Both reactions occur, though cleavage of the oxygen-glycosyl bond predominates (Brandon et al. 1975; Kaylor et al. 1995). Studies performed with di- and trisaccharides as model compounds for cellulose have shown that in all cases an intramolecular nucleophilic substitution reaction causes the mid-chain scission of cellulose, though the actual reaction pathway can vary (Lai 1972; Brandon et al. 1975; Kaylor et al. 1995; Krässig et al. 2004).

Ultimately, mid-chain scission of cellulose will create one new reducing end group and one non-reducing end group. The newly formed reducing end groups will then initiate peeling reactions (Figure 9). The occurrence of this kind of mid-chain scission thereby results in much greater weight losses and thus degradation yields than alkaline degradation only, especially at high temperatures (Corbett and Richards 1957; Lai and Sarkanen 1967).

At low temperatures (< 140 °C), the mid-chain reaction is generally considered as negligible compared to the other reactions, at least on the short term (Haas et al. 1967; Lai and Ontto 1979). Nevertheless, this process has been observed (though at a slow rate) when degrading amorphous cellulose in alkaline solutions at 60 and 80 °C, though not (significantly) with fibrous cellulose (at least not within 1 week). This research therefore indicates that alkaline hydrolysis could occur even at room temperature, though likely at a slow rate. Furthermore, it suggests that the alkaline scission reaction is preferentially occurring in the amorphous cellulose regions, although it cannot be excluded to occur in crystalline regions at a lower rate (Gentile et al. 1987). Nevertheless, since disposal of radioactive waste needs to guarantee safety over the long term, this process might still have a significant effect on the overall long-term degradation rate.

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4 The aglycone is the compound remaining after the glycosyl group of a glycoside is replaced by a hydrogen atom upon cleavage (see Figure 11).
4.1.2 Factors influencing the degradation of cellulose

4.1.2.1 Crystallinity and morphological structure

The overall alkaline degradation of native cellulose is profoundly influenced by its supramolecular structure, since all chemical reactions seem to be rather limited in the crystalline region of cellulose (Haas et al. 1967; Gentile et al. 1987; Helmy 1993; Greenfield et al. 1994b; Klemm et al. 1998; Mittal et al. 2011). The decreased physical accessibility and internal surface area in the crystalline region compared to the amorphous cellulose region (see Section 2.5) play a significant role in this limitation (Gentile et al. 1987). Indeed, peeling, chemical stopping and (at least certain) mid-chain scission reactions are inhibited/delayed by the more highly ordered and rigid physical structure of the crystalline cellulose regions. The majority of degrading molecules is thus terminated to stable, inaccessible reducing end groups in the transition zone from amorphous to crystalline cellulose by physical stopping.

However, the physical properties of cellulose, such as the degree of crystallinity, change strongly upon pretreatment. Indeed, the crystallinity of cotton and wood cellulose generally decreases in the following order: cotton (~70 to 75% CI), (bleached) wood pulp (~60 to 65% CI), mercerised cotton cellulose II (~50 to 55% CI) and regenerated cotton cellulose II (~40% CI) (Jeffries et al. 1969; Ioelovich 2009). Also Fengel et al. (1995) and Mittal et al. (2011) showed the decrease in crystallinity upon transformation of cellulose I to II. Indeed, from 20% up to as much as a two-fold increase in the amorphous content was observed after mercerisation of different sources of native cellulose. Therefore, depending on the (pre)treatment of cellulose, the outcome of chemical degradation (e.g. production of cellulose degradation products) of cellulose with the same origin will vary significantly.

In addition, the morphological structure of the crystalline cellulose regions affect the overall degradation reactions. Studies by Gentile et al. (1987) and Lai and Sarkanen (1967) suggest that though the physical stopping occurs similarly for both cellulose I and II, chemical stopping and mid-chain scission seem to be less drastically inhibited in the cellulose II crystalline regions compared to cellulose I, suggesting a higher accessibility of the hydroxyl groups of cellulose II compared to I. Indeed, mercerised cellulose II has been shown to have a higher internal pore surface area compared to the native cellulose I (see Section 2.5), resulting in a higher accessibility, though still lower than in amorphous domains (Gentile et al. 1987; Fink et al. 1992; Klemm et al. 1998). The higher number of accessible glycosidic bonds inside mercerised cellulose II could therefore lead to a higher degree of chemical degradation reactions compared to native cellulose I.

Nevertheless, although the above-mentioned changes to the structure of cellulose occur upon mercerisation, the overall effect on alkaline degradation of cellulose seems to be rather small, at least at temperatures higher than 140 °C. Based on the results of Lai and Sarkanen (1967), mercerisation does increase the degradation of cotton cellulose (at temperatures above 140 °C and in 5 wt% NaOH for up to 48 hours) consistently, though this increase is not statistically significant. Nevertheless, at such high temperatures, mid-chain scission reactions play a major role in the overall degradation process (see Section 4.1.1.3). As this type of degradation mechanism is less depending on the crystallinity compared to the peeling reactions, the difference in alkaline degradation of cellulose I versus cellulose II at low temperatures cannot be easily extrapolated from the results at high temperatures.

4.1.2.2 Degree of polymerisation

In theory, each cellulose chain has one reducing end group. For a given mass of cellulose, the higher the DP, the lower the number of reducing ends that will be available for the peeling reaction (Richtzenhain et al. 1954; Haas et al. 1967; Van Loon and Glaus 1998). Figure 10 clearly shows the dependence of the maximal amount of cellulose degraded according to the peeling reaction and taking into account stopping reactions, on the degree of polymerisation.
4.1.2.3 pH, alkali concentration and nature

The degradation kinetics of native cellulose are profoundly affected by the concentration of alkali and thus by the pH. At circum-neutral pH, only very slow degradation of cotton hydrocellulose occurs, and up to pH 8.5 this rate is invariable to the pH. However, when the pH exceeds 8.5, the overall degradation rate increases slightly though significantly and linearly with pH, at least up to pH 13.5 (Lai and Sarkanen 1967; Ziderman and Belayche 1978; Lai and Ontto 1979). This pH effect is caused by a combination of the following processes (Ziderman and Belayche 1978; Lai and Ontto 1979):

1. Swelling (and thus inner accessibility) of the cellulose structure, which increases with increasing NaOH concentrations

2. Increased ionisation of the cellulose hydroxyl groups. The peeling reaction can take place with both the mono- and the dianionic intermediate reducing end groups, while the chemical stopping reaction has been shown to occur only at a considerable rate when the alkali concentrations are sufficiently high to produce dianionic intermediates. Increasing the pH would therefore initially result in an increase of the relative rate of peeling versus stopping reaction until a certain pH is reached. Afterwards, increasing the pH would increase the chemical stopping reaction rate as well.

The nature of the alkali cations does not seem to have an effect on the degradation rate. However, different cations present in the degradation solution can affect the degradation products significantly. Indeed, Ca$^{2+}$ ions (or other divalent cations) have been shown to catalyse the benzilic acid rearrangements leading to both ISA and metasaccharinic acid (see Sections 4.1.1.1 and 4.1.1.2), thus enhancing both the peeling and chemical stopping reactions (Machell and Richards 1960b). In the peeling reaction, the presence of calcium results in the preferential production of ISA and reduction of the yield of smaller degradation products. In contrast, when only NaOH is present, additional fragmentation of 4-deoxy-2,3-hexodilulose (see Figure 9) occurs, resulting in the formation of smaller organic acids, as shown in Figure 11 (Whistler and BeMiller 1958; Machell and Richards 1960b; Glaus et al. 1999). However, when Ca(OH)$_2$ is oversaturated in solution, cellulose may be (partially) trapped in the solid Ca(OH)$_2$, resulting in a lower accessibility of the reducing end groups and thus a lower degradation rate (Van Loon and Glaus 1998; Pavadars et al. 2003). Furthermore, because calcium also enhances the chemical stopping reaction, the overall effect of an increasing calcium concentration is a reduction of the overall degradation rate, and extent of degradation (Colbran and Davidson 1961; Van Loon and Glaus 1997).
In a disposal facility, chemical degradation of the cement components of the waste and the repository results in a gradual change in the pore water composition that will be present in and near the waste packages. Initially, the water reaching the cellulose inside the drums will be in equilibrium with the Na and K oxides and with portlandite in the cement, and will therefore contain high concentrations of Na, K and Ca cations while maintaining a pH of ~13.5. Later on, when Na and K oxides are depleted, dissolution of portlandite will control the pH and the chemical composition of the cement pore water, i.e. the pH will decrease to ~12.5 and will contain high concentrations of Ca. When all portlandite has been leached out of the cement, the pore water composition is buffered by other cement phases and the pH drops from 12.5 to 10. When all these phases are completely leached out, the pH drops below 10 (Jacques et al. 2010). Based on calculations taking into account all these stages, the design of the waste repositories (see Section 3.2) and the infiltration of the repository by natural water, we can expect a pH larger or equal to 12.5 inside the monolith at least for as long as the advective water flow is limited (i.e. at least the first 1000 years for surface disposal and longer for geological disposal). During this stage, the composition of the cement water in contact with the cellulose can vary from containing mainly Na, K and Ca to mainly Ca, depending on the type of cement used during conditioning of the cellulose-containing waste (ONDRAF/NIRAS 2019c).

4.1.2.4 Temperature

The extent and rate of cellulose degradation depends on the reaction temperature, as shown in Figure 12 and in several previous studies (Haas et al. 1967; Lai and Ontto 1979; Gentile et al. 1987; Mozdyniewicz et al. 2013). Each of the ongoing degradation reactions is affected by the temperature. At low temperatures (< 140 °C), increasing reaction rates are found for both peeling and stopping reactions with increasing temperature. Due to the higher activation energy for the chemical stopping reaction compared to the peeling reaction, the ratio of peeling to chemical stopping rate constants strongly increases at increasing temperature, which results in an overall higher extent of cellulose degradation with increasing temperature (Haas et al. 1967; Gentile et al. 1987; Mozdyniewicz et al. 2013). On the other hand, at low temperatures (< 140 °C), the mid-chain reaction is generally considered as negligible compared to the other reactions, at least on the short term (Haas et al. 1967; Lai and Ontto 1979). Nevertheless, results obtained by Gentile et al. (1987) showed that mid-chain scission of amorphous hydrocellulose does occur (though slowly) in 1 M NaOH at temperatures below 140 °C, and its rate seems to be increasing as well with increasing temperatures. Overall, these processes result in the observed increase in the degree of degradation with increasing temperatures for a given period of time, as shown in Figure 12. Cellulose degradation rate constants to be used in performance assessment calculations of radioactive waste disposal should therefore be determined under or extrapolated to relevant temperature conditions (e.g. 10 °C for surface disposal).
4.1.2.5 Presence of oxygen

The presence of oxygen during alkaline cellulose degradation does not fully inhibit the degradation process, though it can reduce the overall degradation rate and results in different degradation products. Indeed, when degrading cellulose in 1 to 3 M NaOH in the presence of oxygen and at 179 – 190 °C, only traces of ISA were observed, while large amounts of low molecular weight carboxylic acids were detected (Niemelä 1988). Other studies have also demonstrated that the degradation extent is larger and higher yields of ISA are produced under anoxic conditions compared to aerobic conditions (Kolmodin and Samuelson 1972; Greenfield et al. 1993). Nevertheless, the main degradation pathway is similar for both aerobic and anoxic conditions and at temperatures below 100 °C, i.e. the peeling reaction (Kolmodin and Samuelson 1972).

The formation of high amounts of low-molecular weight organic acids and low amounts of ISA can be explained by the sensitivity of ISA for oxygen. Indeed, Glaus and Van Loon (2009) showed that ISA can decompose in the presence of oxidising agents such as O$_2$ (see Section 5). Furthermore, oxygen can oxidise (part of) the reducing end groups of the cellulose chains, which results in the generation of alkali stable end groups and the termination of the peeling reaction (Päärt and Samuelson 1970; Johansson and Samuelson 1975).

In contrast, the presence of oxygen (or related radicals) at high pressure (e.g. 690 kPa, as tested by De Souza et al. (2002)) can also result in direct oxidation of the outer surface of the crystalline regions (possibly at the position of defects), causing cleavage of the glycosidic bonds, possibly resulting in an increased accessibility of inner cellulose chains. Nevertheless, this process is believed to be rather slow, since it causes only small (though significant) differences to the overall evolution of the crystallinity during degradation of four different types of cellulose in 2.5 wt% NaOH for 90 minutes (De Souza et al. 2002).

Inside the cemented and cellulose-containing waste packages in a repository, the very limited water infiltration will result in a strong limitation of oxygen in the waste packages due to oxygen-consuming processes taking place before the water reaches the monoliths. Anoxic conditions can therefore be assumed during cellulose degradation, at least for as long the monoliths and/or waste packages themselves are not fractured (i.e. first 1000 years for surface disposal and even longer for geological disposal). For surface disposal, degradation of the engineered barriers after more than 1000 years would ultimately lead to more oxic conditions inside (parts of) the repository and likely ultimately even inside the waste when the monoliths loose their physical integrity. It is however difficult to predict when the latter would take place (ONDRAF/NIRAS 2019c).

4.1.3 Modelling of alkaline cellulose degradation

For modelling alkaline cellulose degradation, the 3 main reaction mechanisms need to be taken into account: (1) peeling reaction, (2) stopping reaction (divided into a chemical and physical stopping reaction), and (3) mid-chain scission (see Section 4.1.1). First attempts to describe the alkaline degradation kinetics of cellulose have been reported by Haas et al. (1967), who degraded cellulose with 1.25 M NaOH under anoxic conditions and at temperatures ranging from 65 to 131 °C.

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Figure 12: Dependence of cellulose degradation (indicated as weight loss) on the temperature (data from Haas et al. (1967)). Results shown for cotton cellulose with DP 160, degraded in 5 vol% NaOH under anoxic conditions.
Based on the results of Haas et al. (1967), rate constants for the peeling reaction ($k_p$), for the chemical stopping due to formation of MSA groups ($k_{cs}$) and for the physical stopping ($k_{ps}$) were determined (see Section 4.1.3.1). In addition, reaction rate constants for the mid-chain scission reaction ($k_{ms}$) were derived as well (see see Section 4.1.3.2), based on the work of Franzon and Samuelson (1957), Lai and Sarkanen (1967) and Lai (1972), who studied alkaline degradation of cellulose at high temperatures (148 to 185 °C) and with a range of base concentrations (0.1 to 2.5 M NaOH). Each of these studies focussed on the mid-chain scission reaction by e.g. using reduced cellulose (Lai and Sarkanen 1967) or cellobiose derivatives (Lai 1972) in order to prevent the influence of a primary peeling reaction. These equations were later on applied and elaborated by Van Loon and Glaus (1997; 1998), who studied alkaline cellulose degradation under repository conditions (i.e. in cement-equilibrated water, at pH 13.5 and at room temperature). Note that the solid to liquid ratio was sufficiently high in all studies, which ensures that the NaOH concentration remains practically constant during degradation (i.e. excess of base). This is also the case in disposal conditions, where the pH will remain highly alkaline (> 12.5) for extended periods of time and controlled by an excess of base.

In the sections below, the reaction kinetic equations for each of these reactions are described, which are ultimately used in a model for long-term cellulose degradation, as described in sections 4.1.3.3 and 4.1.3.4.

### 4.1.3.1 Peeling and stopping reaction kinetics

The **peeling reaction** is described according to equation 4, with ($G_e$) the mole fraction of glucose units eliminated, ($G_r$) the mole fraction of reducing end groups available for reaction within a cellulose chain and $k_p$ is the pseudo first order reaction rate constant.

\[
\frac{d(G_e)}{dt} = k_p (G_r)
\]

Equation 4

and

\[
(G_e) = \frac{G_e}{DP_0}
\]

Equation 5

with $G_e$ the number of moles of glucose eliminated per cellulose chain and $DP_0$ is the initial DP of the cellulose chain.

For the **chemical stopping** reaction, the following equation (6) can be written

\[
\frac{d(MSA)}{dt} = k_{cs} (G_r)
\]

Equation 6

with (MSA) the mole fraction of stable MSA end groups formed during chemical stopping and $k_{cs}$ the pseudo first order reaction rate constant for the chemical stopping reaction.

A similar rate equation (7) can be written for the **physical stopping** reaction, though no chemical reaction is involved:

\[
\frac{d(G_{rna})}{dt} = k_{ps} (G_r)
\]

Equation 7

with ($G_{rna}$) the mole fraction of reducing end groups not accessible for peeling reaction and $k_{ps}$ is the pseudo first order reaction rate constant for physical stopping.

Based on equations 6 and 7, the **overall stopping reaction** can be written as:

\[
\frac{d(G_e)}{dt} = (k_{cs} + k_{ps}) (G_r) = k_s (G_r)
\]

Equation 8

with $k_s$ the reaction rate constant for the overall stopping reaction.

At $t=0$, ($G_r$) = ($G_r)_0$, being the initial reducing end group content. Integration of equation 8 gives:

\[
(G_r) = (G_r)_0 e^{-k_s t}
\]

Equation 9

---

5 The solution composition simulates the first stage of cement degradation and contained 0.114 M NaOH, 0.18 M KOH and was saturated with respect to Ca(OH)$_2$ (Van Loon and Glaus 1998).
Substitution of equation 9 in equation 4, followed by integration results in

\[
(G_e) = \frac{k_p^*}{k_s^*} (G_r)_0 (1 - e^{-k_r t})
\]

Equation 10

Based on equation 10, \((G_e)\) reaches a plateau value (see also Figure 10). This plateau value, \((G_e)_{max}\) or \((celdeg)_{ps,max}\), is the maximum amount of glucose units clipped off, taking into account the peeling and the stopping reactions, and can be derived from equation 11:

\[
(G_e)_{max} = (celdeg)_{ps,max} = \frac{k_p^*}{k_s^*} (G_r)_0
\]

Equation 11

As the maximum amount of cellulose degraded depends on the initial mole fraction of reducing end groups in a cellulose chain, it also depends on the initial DP of the cellulose. In theory, each cellulose chain has one reducing end group. However, in reality not all cellulose molecules have reducing end groups since pretreatment processes such as pulping under aerobic conditions could transform reducing end groups into non-reducing end groups. Therefore

\[
0 \leq (G_r)_0 \leq \frac{1}{DP}
\]

Equation 12

and

\[
0 \leq (celdeg)_{ps,max} \leq \frac{k_p^*}{k_s^*} \frac{1}{DP}
\]

Equation 13

These equations are thus in line with the observations that the degradation extent is depending on the DP (see Section 4.1.2.2). The effect of other factors influencing the degradation rate (see Section 4.1.2) can be derived or incorporated as follows:

- **Temperature effect**: the values for the rate constants for the different degradation reactions at varying temperatures below 140 °C are in agreement with the Arrhenius equation (Haas et al. 1967):

\[
k = A e^{-\frac{E_a}{RT}}
\]

Equation 14

with A the Arrhenius parameter and \(E_a\) the activation energy of the reaction. This equation clearly shows the temperature dependence of the degradation reactions (Figure 13) and can be applied to extrapolate the rate constants for lower temperatures (Van Loon and Glaus 1998).

![Arrhenius plot for the peeling off \((k_p)\), chemical stopping \((k_{cs})\) and overall stopping \((k_s)\) reactions of cotton hydrocellulose in 1.25 NaOH, according to data from Haas et al. (1967) and adapted from Van Loon and Glaus (1998). The open symbols represent the experimental data from Haas et al. (1967) and the closed symbols are extrapolated values for 25 °C.](image)
The effect of crystallinity is taken into account by including the physical stopping reaction into the equations.

The effect of pH / alkali concentration or nature was not incorporated in the equations. When using these equations for predicting cellulose degradation under disposal conditions, experimental data of cellulose degradation in cement-equilibrated water are necessary to derive the rate constants. An attempt was made by Van Loon and Glaus (1998) to include the effect of the base concentration in the equations, in analogy to the work of Lai and Sarkanen (1969) on amylose degradation. Based on this, the above-mentioned rate constants can be redefined as OH-dependent rate constants:

\[ k_{i,x} = k_i \frac{K_1 [OH^-]}{1 + K_1 [OH^-]} \tag{Equation 15} \]

with \( k_{i,x} \) as the rate constant of reaction \( i \) at base concentration \( x \), \( K_1 \) the deprotonation constant for the deprotonation of the hydroxyl group on \( C_1 \) of the reducing end group and \( k_i \) the OH-independent reaction rate constants as described in equations 4, 6 and 7. Equation 15 can then be used in equation 13, to derive the maximum degree of degradation. However, these equations only seem valid for base concentrations below 2 M, since at higher concentrations other processes such as swelling of the cellulose also play an important role in the degradation kinetics (Lai and Ontto 1979).

The values for \( k_i \) and \( k_p \) can be derived by fitting the experimental data of produced amount of ISA and/or DOC (dissolved organic carbon) in function of time (Van Loon and Glaus 1998). For the prediction of relatively short-term degradation of cellulose at low temperatures, the above-mentioned model seems to provide a good fit of the experimental results (Mozdyniewicz et al. 2013). An example of this fit is shown in Figure 14.

4.1.3.2 Mid-chain scission reaction kinetics

As mentioned in Section 4.1.1.3, mid-chain scission is also an important reaction mechanism taking part in the overall alkaline degradation of cellulose, though it is considered less important at low temperatures. However, since cellulose degradation kinetics under disposal conditions need to be predicted for several thousands to hundreds of thousands of years, even slow processes might become important on the long term and therefore need to be included.
Although several mechanisms can contribute to the alkaline cleavage of glycosidic bonds in cellulose, each of them applies an internal nucleophilic substitution (Lai 1972; Brandon et al. 1975; Kaylor et al. 1995), which can be expressed in a 2 step reaction mechanism:

\[
R'OR + OH^- \xrightarrow{k_i} R'OR^- + H_2O
\]

\[
k_{ns} \xrightarrow{} R'OH + ROH + H_2O
\]

\[= P + H_2O \quad \text{Equation 16}\]

with R'OR representing chain R' bonded through a glycosidic bond to chain R, P the degradation products, \(k_i\) the deprotonation constant for the glycoside and \(k_{ns}\) is the reaction rate constant of the nucleophilic substitution.

When the base concentration is high enough and the solid/liquid ratio low enough, the hydroxide ions are in excess and will remain constant in time. Therefore, a pseudo-first order reaction can be assumed, according to equation 17 and as proposed by (Lai 1972):

\[
\frac{d(P)}{dt} = k_{ns} (R'OR^-)
\]

with (P) the mole fraction of the degradation products formed by mid-chain scission and (R'OR^-) the mole fraction of ionised intermediate glycosides at time t.

Furthermore, the deprotonation constant \(k_i\) is defined as

\[
k_i = \frac{(R'OR^-)}{[(R'OR)_{i0} - (R'OR^-) - (P)]} \quad \text{Equation 18}\]

with (R'OR)\(_{i0}\) the mole fraction of the protonated glycosides at \(t = 0\).

Combining equations 17 and 18 and integration gives:

\[
\ln \left( \frac{(R'OR)_{i0} - (P)}{(R'OR)_{i0}} \right) = -\frac{k_i k_{ns} [OH^-]}{1 + k_i [OH^-]} t = -k_{ns} t
\]

\[\text{Equation 19}\]

with \(k_{ns}\) the pseudo-first order rate constant of the mid-chain scission reaction.

This equation (19) is in agreement with the study of Franzon and Samuelson (1957) for alkaline degradation of cellulose at 170 °C in 1.25 M NaOH, where the overall degradation was found to be the result of mid-chain scission followed by the endwise peeling reaction. The mid-chain scission is the rate-limiting reaction in this process. The overall degradation rate is conform with the following equation (Franzon and Samuelson 1957; Lai and Sarkanen 1967):

\[
\ln(Y) = -k_{ns} x_n t = -k_h t
\]

\[\text{Equation 20}\]

with Y as the remaining fraction of cellulose left after degradation, \(k_h\) the overall degradation rate constant for mid-chain scission followed by secondary peeling reactions and \(x_n\) the average degradable chain length or the amount of cellulose units peeled off after each chain scission. \(x_n\) was found to be rather constant and independent of the DP, though dependent on the molecular structure and crystallinity of the cellulose (Franzon and Samuelson 1957; Lai and Sarkanen 1967).

Similar as for the rate constants for the peeling and stopping reactions (see Section 4.1.3.1), the effect of the temperature on the overall degradation rate can be observed in an Arrhenius plot, which allows us to estimate the value of \(k_h\) at lower temperatures through extrapolation. Based on the experimental data of Franzon and Samuelson (1957) and Lai and Sarkanen (1967), Van Loon and Glaus (1997) extrapolated a value of \(k_h\) at 25 °C. This theoretical value was about 8 orders of magnitude lower compared to the rate of the peeling off reaction (derived according to Section 4.1.3.1).

Also at high temperatures (thus with important mid-chain scission reaction), the overall degradation rate is linearly depending on the NaOH concentration, at least up to 2 M NaOH (Lai and Sarkanen 1967). To include the effect of the base concentration in equation 20, equation 15 can be applied again (Lai and Sarkanen 1967; Lai and Sarkanen 1969). Furthermore, Mozdyńiewicz et al. (2013) proposed an extended model, which includes more extensive secondary peeling after cellulose chain scission in highly concentrated basic solutions (~4.5 M NaOH). Nevertheless, model (model III in Figure 14) did not provide a significantly better fit of the experimental data (degradation of cellulose at 40 to 60 °C and in 4.5 M NaOH) compared to the model of Van Loon and Glaus (1997), discussed in Section 4.1.3.3.
4.1.3.3 Overall alkaline cellulose degradation kinetics under disposal conditions

Under disposal conditions and thus at low temperatures and at relatively low base concentrations (~0.3 M), it is expected that initially a fraction of cellulose is degraded rapidly through the peeling reaction, in which case ISA is formed. The rest of the cellulose can be assumed to degrade slowly by mid-chain scission followed by peeling reactions of the newly formed reducing end groups. The overall long-term degradation of cellulose under these conditions should thus contain all 3 reaction mechanisms and can be derived when combining equations 10 and 20 into equations 21 and 22 (Van Loon and Glaus 1997):

\[ (Y) = \frac{[1-\frac{k_p}{k_{rs}} (G_r)_0 (1-e^{-k_{rs}t})]}{e^{k_{rs}t}} \]  

Equation 21

and

\[ (celdeg)_t = 1 + e^{-k_{rs}t} \frac{k_p}{k_{rs}} (G_r)_0 (1 - e^{-k_{rs}t}) - 1 \]  

Equation 22

with \( (celdeg)_t \) the overall relative amount of cellulose degraded as a function of time.

The best-fit values of the kinetic rate constants can be derived by fitting the experimental data. These equations fit short-term degradation of cellulose in concentrated NaOH and at 40 to 60 °C nicely (model II in Figure 14B; Mozdyniewicz et al. 2013) and also fit long-term degradation of different sources of cellulose in synthetically prepared cement-equilibrated water\(^4\) and at 25 °C accurately during 12 years as shown in Figure 15 (full lines) (Glaus and Van Loon 2008). Also the new data up to 25 years of degradation are fitted well with the applied model (personal communication L. Van Loon, 2019). Note the differences in reaction rates for the different cellulosic materials. As the environmental conditions were the same for all these experiments, the morphological structure and crystallinity have likely predominantly influenced the degradation rate.
When comparing the best-fit value of $k_h$ at room temperature obtained from 12 year old experimental data (Glaus and Van Loon 2008) to the one theoretically obtained from the Arrhenius equation (Van Loon and Glaus 1997; see Section 4.1.3.2), a significant difference is observed. Indeed, the best-fit value is about 3 orders of magnitude higher compared to the extrapolated value using the Arrhenius equation ($\sim 10^7$ vs $10^{-10}$ respectively). This means that either the extrapolated value for $k_h$ using the Arrhenius equation (see Section 4.1.3.2) is not valid over such a wide temperature range (25 °C vs 140-180 °C) or another not yet known slow degradation process is taking place at low temperatures.

To address this uncertainty, Glaus and Van Loon (2004) performed additional cellulose degradation experiments at elevated temperatures (60 and 90 °C) for 2 years, with the main aim being to verify the obtained Arrhenius relationship between the rate constant for the mid-chain scission and the temperature. They however observed that at elevated temperatures, degradation of cellulose was initially fast for several days, and slowed down over 100 days, but eventually stopped completely when ~60% of the cellulose was degraded. The degradation kinetics were almost identical for the experiments at 60 and 90 °C and independent of the cellulose source and DP. There was no significant indication of ongoing mid-chain scission, for either of the temperatures tested. It should however be noted that the ISA concentrations measured in these experiments increased initially but decreased further over time. The observed decrease was originally attributed to a possible sorption of α-ISA to Ca(OH)$_2$ (Glaus and Van Loon 2004), though it could also be that the test set-up did not provide strict anoxic conditions and part of the ISA was oxidised further (see Section 5; personal communication M. Glaus, 2019). Due to this, the
occurrence of mid-chain scission cannot be ruled out, though neither can the hypothesis of another currently unknown reaction taking place.

Since the evolution of the ISA concentration follows the DOC evolution largely (Van Loon and Glaus 1998; Pavasars et al. 2003), even after 12 years of reaction (Glaus and Van Loon 2008), the peeling reaction seems to provide the final degradation products in both phases of the degradation. Glaus and Van Loon (2008) therefore proposed the occurrence of a decelerated peeling reaction as another possibility for the rate-determining reaction in the second phase of long-term cellulose degradation. In this hypothesised scenario, inaccessible reducing end groups in the crystalline regions of a cellulose chain could become temporarily accessible as reducing end groups in a local amorphous region, which may then undergo peeling. As such a conversion from crystalline to amorphous cellulose has been observed at high temperature and/or in pressurised water, presumably through a paracrystalline state as intermediate phase (Sasaki et al. 2000; Degushi et al. 2008; Kulasekara et al. 2014), such a transformation might also occur under alkaline conditions, though at a slow rate. This process would explain a decelerated peeling such as proposed by Glaus and Van Loon (2008).

In the case of decelerated peeling, the evolution of the mole fraction of reducing groups ($G_r$) can be described as follows:

$$\frac{d(G_r)}{dt} = k_s (G_r) - k_0$$

Equation 23

with $k_0$ the pseudo-zero order reaction rate constant for the rapid peeling reaction when an inaccessible end group becomes accessible.

Integration of equation 23 and combination with equation 4 gives

$$G_r = \frac{k_p}{k_s} (G_r)_0 (1 - e^{-k_s t}) + \frac{k_r k_0}{k_s} t$$

Equation 24

which is similar to equation 10. Also this model provides a good fit with the experimental data (Figure 16) and it is not possible to discriminate, at least on the basis of the long-term experimental data of Glaus and Van Loon (2008), between secondary peeling of cellulose after mid-chain scission or decelerated peeling. It remains therefore still unclear which process is rate-limiting on the long term. Even a combination of mid-chain scission in the crystalline region resulting in inaccessible reducing end groups becoming accessible, cannot be ruled out. Such a mechanism has previously been proposed for hot NaOH attack of cellulose under oxygen-rich conditions, in which case reactive oxygen species can cause mid-chain scissions at the surface of crystalline regions, possibly at the position of defects in the crystalline structure. This chain cleavage then allows some penetration of chemicals further into the crystalline zone (De Souza et al. 2002).

![Figure 16: Extent of cellulose degradation (from Glaus and van Loon (2008)) as derived experimentally for tissues in artificial cement pore water at pH 13.3 and temperature 25 °C and modelled by equation 24 with the following values for the rate constants: $k_p$ and $k_s$ according to Table 1 (values from Glaus and Van Loon (2008)) and $k_0$ 2.9E-9 h⁻¹.](image-url)
4.1.3.4 Long-term predictions of cellulose degradation under disposal conditions

Both Van Loon and Glaus (1997) and Pavasars et al. (2003) proposed predictions of the long-term cellulose degradation in radioactive waste under disposal conditions, using equation 22. In these models, it has been assumed that the overall cellulose degradation is dominated by the peeling reaction in the first years, while slow mid-chain scission reactions become rate-limiting later on and is followed by secondary peeling reactions (Pavasars et al. 2003; Glaus and Van Loon 2008).

To obtain values for the rate constants, both research groups performed long-term experiments (for ~3 years by Pavasars et al. 2003 and over 12 years by Glaus and Van Loon 2008), in which cellulose degradation was studied under similar conditions (see details in Table 1). Although the experimental data of both Van Loon and Glaus (1997) and Pavasars et al. (2003) were rather similar, different values of the reaction rate constants were obtained to fit the experimental data (Table 1). The most important difference is the considerably higher mid-chain scission rate constant applied by Pavasars et al. (2003). However, when the experimental duration is not sufficiently long (i.e. not covering both phases of the degradation process long enough), a variety of numerical values can fit the experimental data within the range of their uncertainty. Indeed, Glaus and Van Loon (2004) showed that decreasing the value of $k_h$ by 5 orders of magnitude still covered the experimental values of Pavasars et al. (2003) completely. A reliable value of $k_h$ can therefore not be derived within the first 3 years of cellulose degradation because the overall reaction rate is largely dominated by the primary peeling reaction. Indeed, Van Loon and Glaus made significant modifications to this value over time (by ~3 orders of magnitude; see Table 1), in order to better fit the long-term experimental data (Van Loon and Glaus 1997; Glaus and Van Loon 2008).

Due to these discrepancies between the parameter values, large differences were found in the long-term prediction of cellulose degradation under disposal conditions (Figure 17). The model of Pavasars et al. (2003) predicts complete cellulose degradation within ~300 to 900 years, even for cellulose with a DP of 10000. On the other hand, using the best-fit parameters for cellulose powder (with DP of 118) of Glaus and Van Loon (2008), complete cellulose degradation only occurs after ~1000 to 5000 years in a cement-based disposal facility.

![Figure 17: Long-term prediction of the extent of cellulose degradation for different degrees of polymerisation according to equation 22, using rate constant values derived by Glaus and Van Loon (2008) at 25°C (A) and Pavasars et al. (2003) at 21 °C (B). Details on the rate constants can be found in Table 1.](image-url)
Table 1: Best-fit parameters for fitting of the data of cellulose degradation experiments obtained in different studies in which cellulose powder was degraded at 25 °C in synthetically prepared cement equilibrated water (see footnote 3). More information regarding the uncertainty on these values can be found in the indicated references.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration experiment</td>
<td>2.6 years</td>
<td>12 years</td>
<td>3 years</td>
<td>3 years</td>
</tr>
<tr>
<td>Cellulose concentration (g L(^{-1}))</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>DP</td>
<td>118</td>
<td>118</td>
<td>348</td>
<td>348</td>
</tr>
<tr>
<td>((G_0))</td>
<td>8.5E-03</td>
<td>8.5E-03</td>
<td>3.4E-03</td>
<td>2.9E-03</td>
</tr>
<tr>
<td>(k_p) (h(^{-1}))</td>
<td>8.5E-03</td>
<td>8.8E-03</td>
<td>1.9E-03</td>
<td>2.1E-03</td>
</tr>
<tr>
<td>((G_0)k_p) (h(^{-1}))</td>
<td>7.2E-05</td>
<td>7.5E-05</td>
<td>6.4E-05</td>
<td>6.1E-05</td>
</tr>
<tr>
<td>(k_s) (h(^{-1}))</td>
<td>3.1E-04</td>
<td>3.2E-04</td>
<td>3.6E-04</td>
<td>4.2E-04</td>
</tr>
<tr>
<td>(k_h) (h(^{-1}))</td>
<td>not taken into account(^a)</td>
<td>1.1E-07(^b)</td>
<td>3.0E-06</td>
<td>2.9E-06</td>
</tr>
<tr>
<td>Remarks</td>
<td></td>
<td>Used for long-term prediction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) the rate of mid-chain scission \((k_h, 5.25E-11 \text{ h}^{-1})\), determined based on extrapolation using the Arrhenius equation as described in Section 4.1.3.2) was believed to be negligible compared to the other degradation reactions (Van Loon and Glaus 1998).

\(^b\) note that the uncertainty on this values is \(\sim\)110%, rendering it less reliable for further calculations.
When applying the model of Pavasars et al. (2003) to the 12-year experimental data of Glaus and Van Loon (2008), it becomes clear that the former does not fit the long-term data accurately and provides an overestimation of the cellulose degradation rate (Figure 15). This model thus underestimates the stability of cellulose because the reaction rate constant that was selected for the mid-chain scission reaction was too high. This however does not necessarily imply that the rate constants derived by Glaus and Van Loon (2008) are correct, but shows that different values of the rate constants can be used to fit certain stages of the alkaline cellulose degradation and only long-term experiments allow us to validate them. Furthermore, another slow reaction could be the rate-determining reaction during the second ‘slow’ degradation phase, instead of mid-chain scission, such as the decelerated peeling reaction proposed by Glaus and Van Loon (2008). At this moment, both possible reaction mechanisms do not offer significantly different long-term predictions (see Section 4.1.3.3), though this should be validated further in the future.

In addition, the cellulose materials in nuclear waste are not consisting entirely of cellulose (e.g. wood also contains lignin and hemicellulose). Depending on the relative cellulose content, the raw materials and the treatments during manufacturing, part of the organic waste will solubilise upon contact with alkaline solutions (i.e. alkali-extractable fraction, mostly hemicellulose\(^6\)), while the cellulose will slowly degrade. Solubilisation of these other organic compounds does not produce additional ISA and is assumed not to affect the overall cellulose degradation rates. Van Loon and Glaus (1998) determined that ~7% of the organic carbon in paper is extractable by contacting the cellulosic material with synthetically prepared cement equilibrated water (pH ~13) for 1 hour, while only ~0.1% of organic carbon in cotton is extractable under the same conditions. These results demonstrate the differences in the relative amount of other C sources present in the cellulosic material. As such large differences can be observed for different cellulose sources, it is not possible to predict the amount of non-cellulose material present in a cellulose-containing waste package.

### 4.1.4 Cellulose degradation products under disposal conditions

Under disposal conditions (room temperature and pH ~13, in cement-equilibrated solution containing NaOH, KOH and saturated with Ca(OH)\(_2\)), ISA is the main degradation product formed during the alkaline degradation of pure cellulose (at concentrations ranging from 5 to 100 g L\(^{-1}\)) and contributes to ~75-83% of the total DOC content after correction for extractable carbon (Van Loon and Glaus 1998; Van Loon et al. 1999b; Pavasars et al. 2003; Glaus and Van Loon 2008; Shaw 2013). This percentage remains stable over time (within the experimental uncertainty), demonstrating that the peeling reaction remains the most dominant process resulting in soluble degradation products, even on the long term (primary vs secondary peeling). When only NaOH is present during cellulose degradation (i.e. simulating the initial period during cement hydration and leaching), the amount of ISA produced decreases to ~30% of the DOC respectively, demonstrating that sodium hydroxide favours fragmentation of 4-deoxy-2,3-hexodilulose into smaller degradation products, while the presence of calcium (or other divalent cations) catalyses the benzilic acid type rearrangement, resulting in the observed enhancement of the ISA production (Machell and Richards 1960a; Greenfield et al. 1993).

Differences in the alkali content could result in differences in the ratio of α- to β-ISA: in the presence of Ca(OH)\(_2\), approximately equal amounts of α- and β-ISA are formed, while in 2 M NaOH, the β-ISA concentration is ~3 times higher than the α-ISA concentration (Feast et al. 1965; Glaus and Van Loon 2008; Shaw 2013).

In addition, other carboxylic acids have been detected during cellulose degradation under disposal conditions (in order of significance): acetic acid, lactic acid, formic acid, threonic acid, glyceric acid, glycolic acid, butyric acid, adipic acid, propionic acid, pyruvic acid and succinic acid. Combined, they represent ~10% of the DOC content (Glaus et al. 1999). Furthermore, metasaccharinic acid, 2,3-dihydroxybutanoic acid, 2-methyl-DL-glyceric acid, dihydroxybutanoic acid, 2-hydroxypentanoic acid, 2,5-dihydroxypentanoic acid, 2,4,5-trihydroxydipentanoic acid, and malic acid have been found by other researchers, though their concentrations are usually low and are not (yet) quantified (Bouwman and Toulhoat 1996; Pavasars 1999; Knill and Kennedy 2003). Lactons of ISA and MSA have been detected as well, though these are likely formed during partial neutralisation of the degradation solution before analysis (Allard et al. 2004).

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\(^6\) Hemicelluloses are naturally occurring branched polysaccharides, i.e. modified xylans, galactoglucomannans, glucomannans and arabinogalactans. Most of them have short chains (DP < 200).
4.2 Radiolytic degradation of cellulose

4.2.1 Reaction mechanisms in dry cellulose

Gamma-irradiation of cotton cellulose results in the production of long-lived and short-lived free radical sites within the cellulose chain R (i.e. initiation step) (Baugh et al. 1967; Ershov 1998):

\[
\text{RH} \xrightarrow{\text{ionizing radiation}} \text{R} + \text{H}
\]

Equation 25

In the absence of water, radical formation due to ionising irradiation of cellulose occurs preferentially by cleavage of the C-1-H or C-4-H bonds of the pyranose ring. Afterwards, some abstraction of hydrogen from other carbon atoms can occur, in which case additional radicals and H\(_2\) (equation 26) would be formed or a migration of the radical along the chain(s) can occur (equation 27):

\[
\text{RH} + \text{H} \rightarrow \text{R} + \text{H}_2 \\
\text{R}^\prime\text{H} + \text{R} \rightarrow \text{R}^\prime + \text{RH}
\]

Equation 26
Equation 27

The resulting radicals are unstable and could undergo homolytic transfer of the radical site towards the opposite side of the glycosidic bond. However, because their structures are strained, they quickly decompose by cleavage of the O-glycoside bond or chain scission (Figure 18). This is believed to be the main cellulose degradation mechanism during ionising radiation (Charlesby 1955; Arthur et al. 1967; Arthur 1971; David and Van den Bergh 1982; Kudoh 2003) and explains the observed decrease in DP with increasing absorbed dose (Figure 19). The formation of the radicals on position C\(_1\) or C\(_4\) is approximately the same, i.e. the radiation-induced cleavage of the C-1-H or C-4-H bonds occurs with about the same probability.

![Radiolytic degradation mechanism in cellulose](image)

Figure 18: Radiolytic degradation mechanism in cellulose, starting with radical formation of C\(_1\) or C\(_4\) by ionising radiation, followed by O-glycosidic bond cleavage (Ershov 1998).

Further cleavage of the pyranose ring results in the formation of reducing end groups. Indeed, Kumakura and Kaetsu (1979) showed that increasing the radiation absorbed dose of cellulose results in an increased yield of reducing glucose end groups. Furthermore, gamma-irradiation of dry wood pulp or cotton cellulose followed by alkaline degradation resulted in an increased production of DOC and of ISA compared to alkaline degradation of non-irradiated dry wood pulp (David and Van den Bergh 1982; Baston et al. 2002).

However, radiolytic degradation of cellulose is not restricted to cleavage of the glycosidic bond within the cellulose chains. The monomer units could also undergo direct radiolytic degradation accompanied by the decomposition of the pyranose ring, which produces additional carbonyl and carboxyl groups as well as H\(_2\), CO\(_2\) and CO (Arthur 1958; Ershov 1998) (Figure 19). These reactions can occur when long-lived radicals are formed on the other C atoms (e.g. C\(_5\) and C\(_6\)) of the cellulose monomers (Baugh et al. 1967). Furthermore, deoxysugars are formed as well, most likely through disproportionation of the terminal radical groups.
Figure 19: Effects of gamma irradiation (expressed as exposure energy) of cellulose in N<sub>2</sub> atmosphere on its molecular properties (Arthur 1958): (A) degree of polymerisation, (B) carbonyl content and (C) carboxyl content. The total absorbed dose (in Gy) of cellulose can be estimated by dividing the exposure energy of gamma irradiation by 100.

The above-mentioned mechanism does not fully explain the production of all observed end products. Therefore, Edimecheva et al. (2005) proposed that also C<sub>2</sub> radicals could be formed (though less frequent compared to on C<sub>1</sub> or C<sub>4</sub>), which could then lead to chain scission and the production of carbonyl groups on C<sub>2</sub>:

\[
\text{Equation 28}
\]

4.2.2 Reaction mechanisms in aqueous conditions

Irradiation of cellulose in an aqueous solution will lead to chemical modifications because of direct and indirect actions of radiation. The direct action is as discussed for dry cellulose (see Section 4.2.1), while the indirect action results from the radicals formed by water radiolysis:

\[
\text{Equation 29}
\]

These radicals (and particularly \(\cdot\text{OH}\)) can then in turn interact with the cellulose polymer by abstracting carbon- or oxygen-bound H-atoms, resulting in the formation of radical functional groups on the cellulose monomers and, depending on the initial radicals, also H<sub>2</sub>O, according to equation 26 and 30 (Jonah and Rao 2001).

\[
\text{Equation 30}
\]

At low cellulose concentration, further propagation reactions can occur, causing predominantly chain scission according to the same mechanism as shown in Figure 18 (i.e. fragmentation / decomposition) or through hydrolysis, leading to the production of additional reducing end groups (Baugh et al. 1967; Jonah and Rao 2001; Gulrez et al. 2011). Free radicals formed upon chain cleavage are readily accessible to interaction with water, resulting in hydrolysed end products and ring opening. In case of a highly alkaline contacting solution, the higher number of reducing end groups would lead to a faster chemical degradation of the cellulose (see Section 4.3).
At higher cellulose load (i.e. aqueous paste-like conditions), a high concentration of radicals, both from water and organics will be formed. Under these conditions, cross-linking and/or branching to form new polymer structures can not be excluded, by way of radical-radical reaction, resulting in the termination of the radiolytic degradation.

Note that due to the higher amount of radicals generated by irradiation in humid conditions (both polymer and water molecules), more recombination of radicals can occur as well, i.e. the probability of terminating the degradation process is higher compared to in dry conditions. This explains why the extent of radiolytic degradation of cellulose by γ-irradiation is similar or even slightly less under humid conditions than under vacuum (observed by Kusama et al. (1976) at dose 1-5 $\times$ $10^4$ Gy, relative humidity 0 to 60% and at room temperature). The production of DOC and ISA by chemical degradation can therefore also be expected to be similar or slightly less for cellulose irradiated under either dry or humid conditions.

4.2.3 Factors influencing the radiolytic degradation rate

4.2.3.1 Morphological and supramolecular structure

Based on electron spin resonance data, molecular weight decreases and molecular weight distribution data of γ-irradiated cellulose (irradiation under vacuum or humid conditions), differences in reaction mechanisms may occur depending on the morphological and supramolecular structure of the cellulose (Baugh et al. 1967; Kusama et al. 1976):

- Crystalline regions of cellulose I are considerably more resistant to radiolytic chain scission compared to the amorphous fraction. However, crystalline cellulose II is significantly more susceptible for chain scission compared to crystalline cellulose I (Kusama et al. 1976; observed after γ-irradiation at dose rate 1 $\times$ $10^4$ Gy h$^{-1}$ for 1 to 5 hours at room temperature).

- Gamma irradiation of cellulose under anoxic conditions not only results in short-lived radicals causing chain scission reactions (as described in Section 4.2.1 and 4.2.2), electron spin resonance data also showed the presence of long-lived free radical sites. For cellulose I, this would occur by dehydrogenation at the C$_5$ position, while in cellulose II, these radicals could be formed by both dehydrogenation at C$_2$ or dehydroxylolation at C$_6$ (Baugh et al. 1967).

- No significant difference between the overall degradation yield (based on chain scission) of γ-irradiated cellulose I and II was found up to doses of 3 $\times$ $10^4$ Gy (under vacuum and at room temperature), though at higher dosages the degradation yield for chain scission of cellulose II increased. The latter could be due to changes in the microstructure of cellulose II induced by the initial radiolytic degradation, causing an accelerated degradation at higher dosages (Kusama et al. 1976).

4.2.3.2 Radiation type and dose

Due to the penetrating power of γ-irradiation, a rather uniform ionisation and radical formation throughout the cellulose fibres can be assumed, though differences between crystalline and amorphous regions occur (see Section 4.2.3.1). For the less penetrating forms of radiation (e.g., α and β), degradation is expected to be heterogeneous (i.e. limited to the surface layer) and dependent on the radiation energy. Little experimental data on the effects of alpha radiation can be found in literature. These data are limited to gas evolution measurements carried out on plutonium-contaminated cellulosic waste in the US. These studies showed that alpha radiation resulted in the production of H$_2$, CO$_2$ and CO, in a similar manner and yield as for γ-irradiation (IAEA 1981).

Based on data from DP changes observed after γ-irradiation of cellulose (under anoxic conditions), a clear relationship of the extent of radiolytic degradation or chain scission with absorbed dose can be observed (Arthur 1958, 1971; Kusama et al. 1976; Ershov 1998; Ponomarev and Ershov 2014) (Figures 19 and 20). Furthermore, the production of carbonyl and carboxyl groups is also linearly depending on the total absorbed dose, at least up to an absorbed dose of 100 kGy (Figure 20).
When high absorbed doses (> 200 kGy) are obtained, the rate of radiolytic degradation is expected to deviate from the linear dependency between the dose and reciprocal of DP (see Section 4.2.5 and Figure 24 for more details). Intermediate and end products then capture electrons, radicals and excitation energy, thereby retarding further degradation of the polymer (Ershov 1998; Ponomarev and Ershov 2014).

In category A waste, the average absorbed dose for cellulose-containing radioactive waste will range from a few kGy up to a few thousands of kGy after 1000 and 5000 years, based on the radionuclide inventory of each type of waste package (based on the data in STOCKDC2, ONDRAF/NIRAS's official database of conditioned waste packages (accessed in Oct 2019)), decay heat and time, and assuming that alpha and beta radiation takes place in the waste itself, while gamma radiation is spread over the entire waste package.

4.2.3.3 Temperature

The rate of radiolytic degradation of cellulose increases considerably with increasing temperature (Ershov 1998), similar to what is observed for alkaline degradation (see Section 4.1.2). Nevertheless, based on Figure 21, it is clear that this temperature dependency is not following the Arrhenius equation over the entire temperature range. At temperatures below 380 K, the yields do not change much when temperature increases, while at temperatures above 380 K, the degradation yield increases markedly with increasing temperature (Ershov 1998). The latter acceleration is likely linked to a faster diffusion of radicals in the polymer, which would enhance the degradation process. At low temperatures, it seems as though the chain scission reaction is not affected considerably, while the further decomposition of the pyranose ring seems to be hampered as the temperature is decreasing, thereby affecting the overall degradation yield (Ershov 1998). To be able to predict the outcome of radiolytic degradation in the waste packages, the degradation rate and yield should be determined at low temperature (< 380 K), since linear extrapolation from data at temperatures above 380 K would result in a significant deviation.
Considering cellulose is not present in heat-emitting waste and temperatures during radiolytic degradation of cellulose are therefore expected to be rather low (−10 to 25 °C), the effect of small temperature changes on the radiolytic degradation rate can be assumed to be rather small.

4.2.3.4 Presence of oxygen

Pending final disposal of cellulose-containing radioactive waste, the waste packages are temporarily stored under atmospheric conditions. During this period, radiolytic degradation of cellulose inside the waste can occur in the presence of oxygen. After disposal, anoxic conditions will prevail inside the waste drum, at least while the monoliths and waste packages themselves remain intact (see Section 3.2).

According to research of Bludovský et al. (1984), the presence of O₂ does not seem to cause changes to the overall reaction mechanism, though it increases the yields of radiolytic degradation products, especially of malonaldehyde, formic acid and other carboxyl groups (increase by more than 50% under oxic conditions). In general, the observed decrease in DP is slightly higher in the presence of oxygen compared to in anoxic conditions (Figure 22), i.e. −10 to 30% higher decrease under oxic conditions than under anoxic conditions, with the difference becoming more severe at higher doses (Arthur 1958; Bludovský et al. 1984). These small differences can be explained by the additional presence of oxygen radicals, which therefore increases the concentration of radicals and enhances the production of certain unstable radicals and/or end products (Bludovský et al. 1984). Nevertheless, the presence of oxygen does not seem to have a considerable effect on the overall extent of radiolytic degradation (Arthur 1958; Bludovský et al. 1984). This is most likely due to the dense packing of the cellulose in the crystalline regions, which hinders the diffusion of oxygen to deeper cellulose chains. In addition, because of the higher concentration of radicals, there is a higher chance of radical recombination in the presence of oxygen (similar to what is observed under humid conditions).
4.2.3.5 Substitution degree of cellulose

For substituted cellulose, the efficiency of polymeric chain scission is determined by the nature of the substituent and the degree of substitution. Substitution of the cellulose chain with additional aromatic groups causes an increase of the radiation stability of the O-glycosidic bond, resulting in a significant decrease of the degradation rate. The extent of the radioprotection by the aromatic groups is depending on the effective number of π-electrons shared within the aromatic group: a decreasing radioprotective effect is observed with decreasing number of π-electrons, possibly as less energy could be absorbed by such aromatic groups upon irradiation (Arthur and Mares 1965; Arthur et al. 1967). A higher degree of substitution also causes a higher degree of radioprotection and a lower degree in random chain scissions as shown in Figure 23 (Arthur and Mares 1965).

Degradation studies with other derivatives of cellulose with ether and ester functional groups also show that the radiolytic degradation extent is decreased due to the presence of these additional groups. However, the extent is largely depending on the type of functional group and the substitution degree. For instance, irradiation of methacryloyl substituted cellulose results predominantly in additional cross-linking of the polymer chains, while mainly chain scission is still observed when irradiating allyl-substituted cellulose (though to a lower extent as for non-substituted cellulose) (Ershov 1998; Gülrez et al. 2011).
4.2.4 Degradation products

The following products were found after ionising radiation treatment of cellulose: H₂, CO, CO₂, carboxyl (formic acid, oxalic acid, glucuronic and gluconic acids) and carbonyl (e.g. acetaldehyde, formaldehyde, acetone, malonaldehyde) compounds, glucose, arabinose, glyoxal, desoxy saccharides, and a series of glucose polymeric compounds ranging from cellobiose to cellohaptaseo (Arthur 1958, 1971; Bludovský et al. 1984; Ershov 1998; Tissot et al. 2013). Although oxygen has little effect on the type of degradation products, its presence does cause an increased product yield, which was particularly the case for the production of formic acid, malonaldehyde and other carboxyl acids, whose production increased by more than 50% under oxic conditions (Bludovský et al. 1984).

Radiation chemical yield (G value) is defined as the number of a particular species produced per 100 eV of energy absorbed by the system from ionising radiation. The G value for the radiolytic degradation products of cellulose can be derived from the linear regression of concentration (in moles per kg cellulose) in function of the absorbed dose (in eV per kg cellulose), in which case the slope of the curve is the G value (Kusama et al. 1976; Bludovský et al. 1984).

According to the general scheme suggested for the radiolytic degradation of cellulose in dry conditions and under anoxic atmosphere (see Section 4.2.1), the following yield of the main products can be expected:

\[ 2G_{H_2} \equiv G_d \cong G_{RCHO} \equiv G_{CO_2} + G_{CO} \]  

Equation 31

with G_d the overall degradation yield (i.e. the yield of glycosidic bond scissions).

This equation (31) indicates that each cleavage of the polymeric chain is accompanied by the formation one CO₂ or CO molecule and one carbonyl group (Ershov 1998). Furthermore, Figure 20 shows that radiolytic cellulose degradation under anoxic conditions generates more carbonyl compounds compared to carbonyl compounds, i.e. the carbonyl group yield is equal to 5.2 to 7.0, while that of carboxyl groups ranges from 0.9 to 3.3 (Arthur 1958; Bludovský et al. 1984; Ponomarev and Ershov 2014). It has been observed, however, that the carboxyl yield is similar to the carbonyl yield after irradiation in oxygen (Bludovský et al. 1984). G values for the production of H₂, CO, CO₂ by γ-irradiation of dry cellulose under anoxic conditions are ranging from 0.7 to 3.2, 0.9 to 3.2, and 1.5 to 6.0 respectively (Ershov 1998; Arthur 1971).

Although G_H₂ values for γ-irradiation of cellulose are uniform, for α-irradiation, the G_H₂ values vary somewhat, depending on how closely cellulose is in contact with the alpha emitter, and also on the thickness of the cellulosic material. These G_H₂ values are not dose rate dependent, although for very high dose rates, some localised matrix depletion near individual alpha emitting particles could occur (IAEA 1981).

4.2.5 Modelling of radiolytic degradation of cellulose

In general, radiolytic degradation of cellulose can be predicted by considering only random chain scission as the reaction mechanism and assuming crosslinking due to irradiation as negligible. Early research was performed by Arthur (1958) who studied the decrease in DP of cellulose in air or under nitrogen atmosphere at different dosages of γ-irradiation. Based on his results (e.g. Figure 19), the following equation was established, indicating the dependence of the DP on the absorbed dose:

\[ \ln DP = a \ln D + b \]  

Equation 32

with D the total absorbed dose, a and b the slope and intercept of the logarithmic plot of the DP in function of D. However, this equation does not allow for a direct calculation of the overall radiolytic degradation yield.

For linear polymers such as cellulose, the individual polymer chains rarely have exactly the same DP and thus molecular masses, i.e. there is always a distribution of the molecular masses around an average value (see Section 2.1). The molecular mass distribution of a polymer describes the relationship between the number of moles of each polymer chain with a certain DP and the molecular mass of these chains. It is often described by the ratio of the weight-average molecular weight to the number-average molecular weight (see equations 5 and 6). For a most probable molecular mass distribution, M_w / M_n should be 2 (Kusama et al. 1976).

To describe the kinetics of radiolytic degradation of cellulose, its molecular mass distribution is assumed the most probable one and the chain scission to occur randomly. In that case, the molecular mass distribution will be maintained, while the average molecular mass of the fragments decreases. Based on these assumptions, a statistical approach was deduced to describe the radiolytic degradation of cellulose in function of the dose (Horio et al. 1963; Kusama et al. 1976; Ershov 1998).
In this statistical approach, Charlesby (1955) deduced the number of chain scissions (S) directly from the change in DP, which was later on elaborated by Horio et al. (1963):

$$\frac{1}{DP} - \frac{1}{DP_0} = \frac{S}{N}$$

Equation 33

with N being the number of monomer units, which is approximately the total number of glycosidic bonds between monomers. S/N therefore gives the fraction of bond scissions.

On the other hand, S is also related to the radiation dose D, which can be written as:

$$S = N p D^c$$

Equation 34

with p the probability of bond scission occurring per unit of radiation dose and c is a constant, derived from experimental data, but frequently assumed to be 1 (e.g. Kusama et al. 1976).

When combining equations 33 and 34, the following relationship between degree of polymerisation and radiation dose is given:

$$\frac{1}{DP} - \frac{1}{DP_0} = p D^c$$

Equation 35

The number of scissions can also be calculated from the yield of radiolytic degradation according to the following equation (Ershov 1998):

$$\frac{S}{N} = \frac{D DP_0 m G_d}{10^2 N_A}$$

Equation 36

with m the molecular mass of the cellulose monomeric unit and $N_A$ Avogadro’s number.

When combining equations 32 and 35, the following relationship between the reciprocal of DP and the total absorbed dose was found by Ershov (1998), which is similar to equation 34, though incorporates measurable parameters. This results in a relationship that is easier to validate experimentally and is for instance in agreement with Figure 20.

$$\frac{1}{DP} - \frac{1}{DP_0} = \frac{G_d m D}{10^3 N_A}$$

Equation 37

Based on this equation and experimental data, the overall degradation yield $G_d$ (i.e. yield of chain scission events) can be calculated. From this, the average radiolytic degradation rate can be calculated by multiplying the $G_d$ value with the applied dose rate.

Although usable, equations 33 to 37 were all obtained for polymers with the most probable molecular mass distribution. However, this is generally not the case for natural cellulose. Nevertheless, as radiolytic degradation results in random chain scissions, it will ultimately lead to the most probable distribution. Therefore, these equations are only valid for a radiation dose as from 30 to 80 kGy depending on the initial molecular mass distribution (Ershov 1998). This was confirmed experimentally by Kusama et al. (1976), who found that the most probable distribution was reached at an absorbed dose of 30 to 50 kGy.

Based on experimental data of radiolytic degradation of cellulose by γ-irradiation in the absence of oxygen and at room temperature, $G_d$ values for chain scission are found to be in the range of 2.8 – 6.0 (when considering only cellulose with the most probable molecular mass distribution) (Kusama et al. 1976; Ponomarev and Ershov 2014).

### 4.3 Combined radiolytic and alkaline degradation of cellulose

As shown in previous sections 4.1 and 4.2, a considerable amount of work has been carried out to investigate the rate of alkaline degradation of cellulose and to study the effects and yield of radiolytic cellulose degradation. However, only few studies have been performed to investigate the effect of ionising radiation on the alkaline degradation of cellulose. Baston et al. (2002) demonstrated that the degradation extent of cellulose (paper tissues) under alkaline conditions increases (i.e. increased production of DOC) with increased total absorbed dose delivered by γ-irradiation (up to ~230 kGy absorbed dose).

The CDPs produced by the combined radiolytic and alkaline degradation of cellulose are similar to those produced by alkaline degradation alone, though the production rate is higher. In addition, David and Van den Bergh (1982) showed that the
weight loss by instant (i.e. within 2 hours) alkaline cellulose (both I and II) degradation increased when the cellulose was pre-irradiated with γ-rays (Figure 24). This indicates that alkali-soluble and/or easily chemically degradable organics are formed during irradiation, as discussed in Section 4.2.4. Furthermore, also the production of ISA was enhanced: γ-irradiation at 5 kGy increased the ISA concentration formed by instant alkaline degradation by a factor 17 to 19 (David and Van den Bergh 1982). Based on this research it is to be expected that the ionising radiation of cellulose inside a waste package will lead to radiolytically degraded cellulose, which is more susceptible towards alkaline degradation. This will likely lead to an enhancement in the overall degradation of cellulose, compared to alkaline degradation only. Note however that long-term degradation experiments investigating the combination of both degradation processes have not been performed (yet).

Figure 24: Extent of radiolytic degradation of cellulose I expressed as weight loss of the solid phase after 2 hours of degradation in alkaline solutions (indicated in legend). The cellulose used was wood pulp for paper making purposes. Data obtained from David and Van den Bergh (1982).
5 Chemical stability of ISA

Investigations into the chemical stability of ISA have been carried out scarcely in the past. During several studies, chemical transformation of ISA was observed in the presence of oxygen, when ISA was dissolved in solutions with CaO or in cementitious water with/without additional cement paste or Ca(OH)$_2$ as a solid phase, at temperatures up to 190 °C and under reduced or atmospheric pressure. The end products of this reaction were formic, glycolic, lactic and acetic acid (Bernhauer and Wolf 1930; Hurdus and Pilkington 2000; Glaus and Van Loon 2009). Furthermore, Alfredsson et al. (1961) and Feast et al. (1965) detected a significant decrease in ISA concentration under oxic and alkaline conditions at 100 to 170 °C, although they could not identify the reaction products.

One rather extensive experimental study performed by Glaus and Van Loon (2009) focussed on the decomposition of α-ISA in heterogeneous alkaline systems containing either Ca(OH)$_2$ (25 to 100 g dm$^{-3}$, present as solid phase) or cement paste, which was monitored at room or elevated temperatures and for up to 250 days. This study demonstrates that the presence of oxidising agents such as O$_2$ causes a significant conversion of α-ISA, whereas only limited amounts of α-ISA are converted under anoxic conditions (especially during the first days of the experiment) (Figure 25). In the latter case, it was hypothesised that either traces of oxygen remained bound to the solid phases or other unidentified oxidising impurities could be responsible for the reactions observed. Note however that the reaction only seems to take place significantly when O$_2$ is present in stoichiometrically equivalent amounts (Figure 25). This explains why other studies did not detect ISA decomposition under anoxic conditions (Van Loon and Glaus 1998; Hurdus and Pilkington 2000) or during long-term anoxic alkaline degradation of cellulose (Glaus and Van Loon 2008).

![Figure 25: Concentration of α-ISA (A) and its reaction products (B) in artificially prepared cement water with 100 g dm$^{-3}$ Ca(OH)$_2$, to which a certain amount of O$_2$ was added (according to legend) after ~40 days. The reaction temperature was 28 °C. (Glaus and Van Loon 2009).](image)
6 Conclusions

As one of the most abundant organic materials used on earth, cellulosic materials make up a significant part of the Belgian radioactive waste. Under the anoxic and alkaline conditions of a cementitious repository and/or in the presence of a radiation field, cellulose is susceptible to degradation processes, which result in the formation of soluble cellulose degradation products. Under the existing disposal conditions, these degradation products could enhance the transport of certain radionuclides. Therefore, investigation of the reaction mechanisms and kinetics of such degradation processes is of high interest for safety assessment calculations. In this report, the current knowledge regarding cellulose degradation under radioactive waste repository conditions has been discussed.

Under disposal conditions (i.e. pH > 12.5; low temperature; anoxic conditions), chemical degradation of cellulose can take place via different reaction mechanisms. Initially, the amorphous regions of cellulose will degrade rapidly through endwise depolymerisation or peeling of the reducing end monomer units. Simultaneously, a chemical stopping reaction will take place, resulting in the production of a non-reducing end group at the end of a cellulose chain, thereby blocking the continuation of the peeling reaction. Furthermore, when the peeling reaction reaches the more ordered crystalline regions of the cellulose, the reaction is stopped by the inaccessibility of the reducing end group (i.e. physical stopping). Finally, an additional mid-chain scission reaction is known to take place in cellulose chains at high temperatures (> 140 °C), but might also occur at low temperatures. Though the rate is assumed rather low at disposal temperatures, on the long term this reaction could still be important, since it generates new reducing ends at the cleaved sites of the original cellulose chain, and can thereby restart the peeling reaction. This reaction would therefore become more important once the initial peeling reaction and thus fast cellulose degradation rate slows down. Nevertheless, a unknown chemical reaction, which would ultimately also start a secondary peeling reaction, cannot be ruled out either (e.g. decelerated peeling).

Furthermore, due to the presence of radionuclides in the waste, radiolytic degradation of cellulose will occur as well. The main radiolysis reaction taking place in cellulose is the chain scission reaction, which generates two smaller chains with one of them having a new reducing glucose end group. Due to this, additional alkaline degradation is expected when cellulose within radioactive waste is exposed to cement-equilibrated water within the disposal facility. The occurrence of radiolytic chain scission reactions prior to or during alkaline degradation could be considerably faster and thus more important compared to the alkaline chain scission or another unknown slow chemical process, thereby rendering the chemical chain scission as negligible on the long term. Nevertheless, additional experimental data investigating the long-term effect of irradiation on the extent and rate of alkaline degradation are required.

Degradation of cellulose will generate a wide range of low molecular weight organic compounds, of which isosaccharinic acid is the most abundant and relevant for radionuclide mobilisation. The presence of Ca in the cement-equilibrated water in the disposal facilities will catalyse the production of isosaccharinic acid as the main product of the peeling reaction (~80% of the DOC), although other low molecular weight organics will also be formed. Two stereoisomers of ISA (α and β) are produced, at more or less equal amounts in cement-equilibrated water. As cellulose degradation products and especially ISA can form complexes with certain radionuclides, their presence in the radioactive waste could enhance the transport of the radionuclides through the disposal facility towards the surrounding environment.

In the past, research has been performed to model the degradation of cellulose, either through chemical or radiolytic degradation processes. These models allow us to make a prediction of the (long-term) degradation of cellulose under disposal conditions, either by alkaline degradation or by radiolytic degradation. For alkaline degradation, the current model proposed by Glaus and Van Loon (2008) seems to fit the long-term data (12 years) nicely and therefore seems to provide a rather accurate prediction of the long-term behaviour. However, the lack of suitable data for and the remaining uncertainty on the rates of the mid-chain scission reaction at low temperature, or further knowledge regarding the possibility of another slow chemical reaction taking place, make predictions of the long-term extent and overall rate of degradation rather uncertain. Models for radiolytic degradation have been developed as well, based on the assumption that only random chain scission reactions are taking place (e.g. Ershov 1998), but are not (yet) validated for long-term processes (i.e. at increasing absorbed doses). Furthermore, a model containing the combination of both degradation processes is still lacking and is definitely needed to be able to predict the long-term degradation of cellulose under disposal conditions. Indeed, as radiolytically induced chain scission would enhance the alkaline degradation of cellulose, both processes are important and should be included in a combined model. This model would then allow us to make a more reliable long-term prediction of cellulose degradation under disposal conditions.
7 References


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