ELSEVIER

Carbohydrate Polymers 51 (2003) 281–300

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Degradation of cellulose under alkaline conditions

Charles J. Knill, John F. Kennedy*

Birmingham Carbohydrate and Protein Technology Group (BCPTG), Chembiotech Laboratories, Institute of Research and Development, University of Birmingham Research Park, Vincent Drive, Birmingham B15 2SQ, UK

Received 4 October 2001; revised 16 May 2002; accepted 13 June 2002

Abstract

A review of the important area of cellulose degradation under alkaline conditions is presented; it focuses on its relevance to the possible disposal of radioactive wastes in an underground repository in which cement-based waste encapsulation grouts and backfill may be employed. An overview of the alkaline degradation pathways of monosaccharides and substituted monosaccharides is initially presented, before progressing to the reactions involved in the alkaline degradation of cellulose, namely end-wise degradation, termination, alkaline scission, and oxidative alkaline degradation. Physical factors affecting reaction rates and the alkaline degradation of hemicellulose are also discussed. A review of the identity of the commonly detected alkaline degradation products (and their numerous synonyms) is presented, along with discussion of the rates of degradation of cellulose. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Alkaline; Cellulose; Degradation; Peeling; Saccharinic acids

1. Introduction

A consultation process into possible options for the long-term management of radioactive waste in the UK is currently underway (DEFRA, 2001). One option for the long-term isolation of radioactive waste from the accessible environment is to place these wastes in a repository excavated in stable rock formations, deep underground (deep geological disposal). A multi-barrier concept has been developed by Nirex for a deep underground repository for the disposal of solid intermediate-level (ILW) and certain low-level (LLW) radioactive wastes making use of both engineered and natural barriers to form a containment system (Nirex, 2001a). Such a repository would be carefully designed and engineered to provide deep, excavated vaults together with the necessary access ways. Typically, wastes would be packaged in steel or concrete containers, usually with a cement grout (Atkins & Glasser, 1992), and subsequently placed in the vaults. Some time later, the vaults would be backfilled with a cement-based material, the Nirex Reference Vault Backfill (NRVB) (Francis, Cather, & Crossland, 1997; UK Patent, 1997), completely surrounding the waste packages. Engineered barriers would be provided by the cement grout, the containers and the backfill, and natural barriers by geological formations that surround the repository and that lie between the repository and the accessible human environment.

An important component of research in support of the development of this repository concept is the consideration of the safety of a repository once operations have ceased and the repository has been closed (post-closure performance). Such work is supported by the Nirex Safety Assessment Research Programme (NSARP), which is currently carrying out generic, non-site specific, research into options for the long-term management of radioactive wastes. Part of the NSARP is concerned with processes that occur in the vaults and their contents (collectively known as the 'near field') relevant to the performance of near-field barriers and radionuclide migration (Chambers, Williams, & Wisbey, 1995).

Following closure of a repository based upon the Nirex disposal concept and subsequent resaturation of the repository by ingressing groundwater, a high-pH, chemically reducing environment is expected to arise and be maintained (Askarieh, Chambers, Hickford, & Sharland, 1998; Chambers et al., 1995). Resaturation may occur over a few decades following repository closure (Baker et al., 1997). The dissolution of calcium hydroxide from the NRVB would give long-term porewater pH values of 12.5 (at 25 °C). Peak temperatures at the centre of a vault of around 60 °C would occur within 4 months of backfilling. However, the maximum temperature within disposal vaults

* Corresponding author. Tel.: +44-121-414-7029; fax: +44-121-414-7030.

0144-8617/03/$ - see front matter
PII: S0144-8617(02)00183-2

is expected to fall to below 50 °C in approximately 1 year post-closure. Then remain at about 30 °C for over 1000 years, returning to the temperature of the pre-existing host rock in 100,000 years (Askarieh & Worth, 1999).

The solubilities and sorption of radionuclides are important data in representing their behaviour in assessment calculations of the post-closure performance of a repository for the deep disposal of radioactive wastes (Baker et al., 1997; Nirex, 2001b). It is therefore necessary to consider any effects that may influence the solubility and sorption of radionuclides. One possible influence is the formation of water-soluble complexants by the degradation of the solid organic polymers present in ILW and LLW. This may occur by radiolytic, chemical or microbial degradation under repository conditions (Greenfield, Rosevear, & Williams, 1990).

Early experimental work examined the radiolytic and chemical degradation of a range of organic materials likely to be present in radioactive wastes and the effects on concentration of plutonium in solution. It established that the chemical degradation of cellulose under alkaline, anaerobic conditions was particularly important (Bradshaw et al., 1987, 1986). Although radiolysis of cellulose is known to occur (Arthur, 1971; David & Van den Bergh, 1982), the magnitude of the effect of chemical degradation of cellulose under alkaline conditions on plutonium concentration masked any potential contribution from radiolytic degradation (Bradshaw et al., 1987, 1986). Investigations in the 1950s and 1960s into the effects of radiation on cellulose demonstrated that the principal effects of γ-irradiation of cotton cellulose are oxidation to yield reducing groups, chain cleavage, and formation of carboxyl groups, in the approximate ratio of 20:1:1 (Arthur, 1958; Bellamy & Miller, 1963; Blouin & Arthur, 1958).

Cellulosic wastes, including paper, tissue, filters, cloth and wood, form a significant proportion of the organic materials in ILW in the UK (Ilett, Pilkington, & Tweed, 1998). The common feature of these is that they contain polysaccharides, with cellulose being by far the major constituent. Studies in the NSARP of the effects of chemical degradation of cellulose were therefore extended. These showed that the solubility or sorption behaviour of a number of radionuclides was affected by leachates from the anaerobic alkaline degradation of cellulose (Baston, Berry, Bond, Brownsword, & Linklater, 1992; Biddle, Greenfield, Pilkington, & Spindler, 2000; Greenfield, Hurdus, Pilkington, Spindler, & Williams, 1994; Greenfield, Hurdus, Spindler, & Thomason, 1997; Greenfield et al., 1995; Harrison, 1991; Moreton, 1993). Similar investigations have been carried out by other workers (Bourbon & Toulhoat, 1996; Rai, Rao, & Moore, 1998). From the results of such studies it is possible to incorporate the effects of cellulose degradation products in performance assessment calculations (Nirex, 2001b).

As these studies have shown the ability of the complexants arising from the alkaline degradation of cellulose to mobilise radionuclides, a detailed understanding of the chemical degradation pathways and mechanisms is important. Obviously such effects are dependent upon the levels of potential cellulose degradation products present in the repository as a function of time, i.e. the predicted rate of cellulose degradation in the repository is also important (Askarieh et al., 2000).

The main part of this review therefore focuses upon the products arising as a result of the degradation of cellulose under alkaline, anaerobic (post-closure) conditions, at temperatures <170 °C, since these conditions predominate with respect to the long-term repository environment. Products that may be obtained under other conditions that may be experienced by the waste prior to closure of the repository (e.g. aerobic oxidative degradation) are also discussed.

The action of alkali upon monosaccharides and substituted monosaccharides is discussed initially, since this provides the necessary background information with respect to the types of reactions involved in polysaccharide degradation mechanisms. Different nomenclature regimes are often utilised to describe the same compound. This is definitely the case with respect to the alkaline degradation products of carbohydrates where numerous names are regularly used (often interchangeably), thereby making reviews of the scientific literature all the more difficult. The degradation products presented in this review are generally referred to by their systematic names. However, synonyms (e.g. trivial names) are also used where appropriate since they are routinely utilised in carbohydrate chemistry due to the inherent complexity of the corresponding systematic names (the final data table includes all names/synonyms of observed degradation products).

As mentioned above, radiolytic and microbial degradation of cellulosic materials may also occur in a repository. Further detailed discussion of these topics is beyond the remit of this review. For further information on such topics, readers are referred to several articles which cover all aspects of cellulose degradation mechanisms (including alkaline, radiolytic, acidic, enzymatic and mechanical degradation) (Blazej & Kosik, 1985; Blazej, Kosik, & Spilda, 1990; Greenfield, Harrison, Robertson, Somers, & Spindler, 1993; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998; Lai, 1991; Meller, 1960a,b; Nevell, 1985a; Phillip, 1984; Redfern, 1996; Richards, 1971; Whistler & BeMiller, 1958).

The microbiology of waste repositories has been considered in the NSARP (Coutts et al., 1997; Grant, Holtom, Rosevear, & Widdowson, 1997) and elsewhere (Arter, Hanselmann, & Bachofen, 1991; Bachofen, 1991; Christofi & Philp, 1991; McKinley & Grogan, 1991). Microbial action on cellulosic wastes or their degradation products can lead to the production of gas (Agg, Cummings, Rees, Rodwell, & Wikramaratna, 1996).

2. Alkaline degradation of monosaccharides

The basic principles of the complex field of monosaccharide degradation by alkali, namely the tautomerism of aldoses and ketoses with enediols, were established by Nef (1907, 1910) and Nef, Hedenburg, and Glattfeld (1917), who proposed that reactions took place in two major steps: (i) isomerisation of the monosaccharide, with loss of water, to an α-dicarbonyl intermediate, followed by: (ii) benzilic acid type rearrangement to produce acidic degradation products. However, many years previously, Peligot (1839, 1880a,b) reported that an acid was among the products detected when glucose was subjected to the action of barium hydroxide or calcium hydroxide (Sowden, 1957), and isolated the first crystalline lactone (namely α-D-glucosaccharin), but thought that it was an isomer of sucrose and therefore named it saccharin, and the corresponding free acid saccharinic acid. This area was deemed to be too complicated by many researchers and was therefore largely neglected until renewed interest many years later.

Several theories were proposed to explain experimental findings. However, the first theories that attempted to rationalise such observations on carbohydrates heated in alkaline solution were made by Evans and co-workers (Evans, 1942; Evans & Benoy, 1930; Evans & Hockett, 1931; Gehman, Kreider, & Evans, 1936), who proposed a mechanism based upon the alkaline degradation of maltose. This mechanism proposed that a (1 → 4)-linked disaccharide undergoes reverse aldol condensation to give several smaller components, which are capable of further alkaline degradation to produce saccharinic, lactic and other acids (Corbett, 1959). However, there was insufficient evidence that the presence of a double bond in an enediol structure weakened a glycosidic linkage in the α-position.

Pacsu studied the degradation of periodate-oxidised cellulose using sodium hydroxide (1 M) at room temperature and observed that the oxidised cellulose had been degraded to acidic products of low molecular weight (Corbett, 1959). The mechanism proposed by Pascu to explain these observations was based upon the assumption that all oxidising agents attacked cellulose in a manner similar to that of periodic acid. However, the assumption was invalid because there was no evidence that all oxidations occurred via glycol cleavage.

Isbell (1944) suggested a reaction mechanism, which was a modified version of the earlier reaction mechanism suggested by Nef (1907), to explain the production of saccharinic acids when carbohydrates were treated with alkali (Corbett, 1959; Sowden, 1957). The Nef–Isbell mechanism for the alkaline degradation of D-glucose (**1**) is shown in Fig. 1. The first step in the sequence involves the production of an enediol (**2**), via keto–enol tautomerism (i). This is followed by the production of an enediol anion (**3**) via deprotonation by hydroxide ions (ii). Anion isomerisation (iii) then takes place resulting in a mixture of equilibrium intermediate anions (**3**–**5**).

An important consequence of anion formation is the destruction of chirality at the C-2 position, i.e. reprotonation of anion (**3**) followed by conversion to the aldose form (via keto–enol tautomerism) results in the generation of D-glucose and its C-2 epimer (D-mannose). Similarly, protonation of anion (**4**) results in the production of D-fructose. Therefore, the initial phase of the alkaline degradation of D-glucose in aqueous media results in the formation of a mixture of D-glucose, D-mannose and D-fructose. This was first observed by Lobry de Bruyn and Alberda van Ekenstein (1895a,b, 1897) and the process is generally referred to as the Lobry de Bruyn/Alberda van Ekenstein transformation (Speck, 1958). Anion (**5**) is not involved in these early stages of degradation since it is formed more slowly and is therefore present at a significantly lower concentration than the other anions present (**3** and **4**).

Anions (**3**–**5**) then undergo β-hydroxycarbonyl elimination (iv), i.e. elimination of the hydroxyl group in the β-position to the negatively charged (carbonyl) oxygen. This results in the formation of a diketodeoxyglycitol, i.e. introducing α-carbonyl functionality relative to the enol arising as a result of the β-elimination (**6**–**8**). The corresponding vicinal dicarbonyl compounds (**9**–**11**) are then produced via keto–enol tautomerism (v), and in the final stage of the Nef–Isbell mechanism they (**9**–**11**) then undergo a benzilic acid rearrangement (vi) to produce the corresponding deoxyaldonic (saccharinic) acids (**12**–**14**). Thus, anion (**3**) produces a mixture of 3-deoxy-D-ribo-hexonic and 3-deoxy-D-arabino-hexonic acids (**12**), formerly known as D-glucometasaccharinic acid (Machell & Richards, 1960c). Anion (**4**) produces a mixture of 3-deoxy-2-*C*-(hydroxymethyl)-D-erythro-pentonic and 3-deoxy-2-*C*-(hydroxymethyl)-D-threo-pentonic acids (**13**), formerly known as D-glucoisosaccharinic acid (Machell & Richards, 1960a,b). Anion (**5**) produces a mixture of 2-*C*-methyl-D-erythro-pentonic and 2-*C*-methyl-D-threo-pentonic acids (**14**), formerly known as D-glucosaccharinic acid.

Alternatively the diketodeoxyglycitol intermediates can undergo alkaline cleavage yielding carboxylic acid and aldehyde fragments. Likewise, various intermediates can undergo reverse aldol condensations, liberating smaller fragment molecules with aldehyde functionality. Thus, the second sequence of reactions involves aldol condensation of products containing aldehyde functionality, whereby tetroses, pentoses, and $>C_6$ sugars and their deoxy derivatives may be formed. All such generated sugars can then participate in the first sequence of reactions detailed previously. Aldol and reverse aldol condensations are significant side-reactions in such alkaline reaction mixtures because of the pronounced catalytic effect of hydroxide ions with respect to such reactions (Speck, 1958).

Research in more recent times has focused upon understanding the fundamental aspects of the alkaline degradation of monosaccharides in aqueous solution (de Bruijn, Kieboom, & van Bekkum, 1986). In summary, the

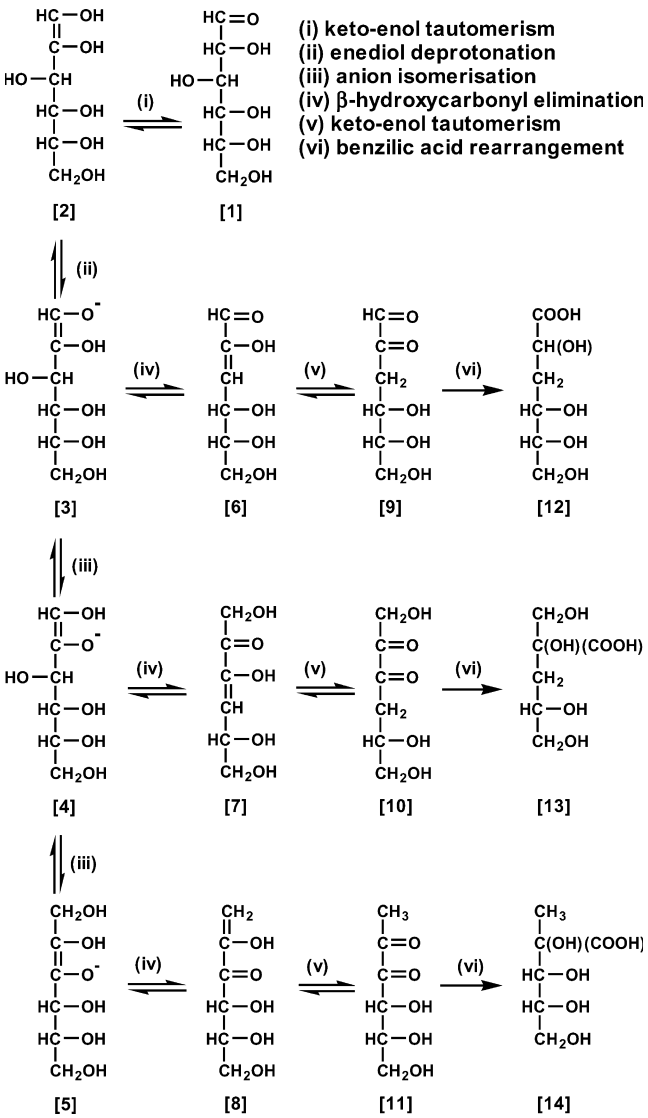


Fig. 1. Nef–Isbell mechanism for the alkaline degradation of D-glucose (**1**).

alkaline degradation of hexoses results in reaction products consisting principally of numerous acids ($\leq C_6$), e.g. the six-carbon deoxyaldonic acids (saccharinic acids) (Sowden, 1957). Higher molecular weight compounds ($>C_6$ acids), and miscellaneous non-acidic and cyclic unsaturated carbonyl compounds are also formed in minor amounts (Forsskåhl, Popoff, & Theander, 1976; Theander & Nelson, 1988). The mechanisms by which the numerous alkaline degradation products are formed are beyond the scope of this review, however, the reader is pointed in the direction of several articles that provide information on this area (Greenfield et al., 1994; Machell & Richards, 1960a,b; MacLeod & Schroeder, 1982; Sowden, 1957; Speck, 1958).

The relative composition of the alkaline degradation products is influenced by several reaction parameters, e.g. temperature, the nature and concentration of the alkali, and the monosaccharide substrates present (de Bruijn et al., 1986; de Bruijn, Kieboom, & van Bekkum, 1987a,b; de Wit, Kieboom, & van Bekkum, 1979). In summary: (i) an increase of hydroxyl ion concentration and the use of divalent cations favours the formation of 2-hydroxypropanoic acid (lactic acid) and decreases the amount of methanoic acid (formic acid), 2,3-dihydroxypropanoic acid (glyceric acid) and the total amount of C_4–C_6 acid products; (ii) the composition of reaction products is the same at either 5 or 80 °C, i.e. is independent of temperature; (iii) alkaline degradation of dilute solutions (1 mM) results in almost complete conversion of the monosaccharides into $\leq C_6$ acids; (iv) higher molecular weight compounds are found to be increased at pH 11–12 and at higher monosaccharide concentration (0.1 M).

Yang and Montgomery (1996) identified the alkaline degradation products arising from the incubation of D-glucose with calcium hydroxide at equimolar ratios at different concentrations (1.8–50% w/w, 30 min, 100 °C). In their studies, D-glucose (0.1 M) in aqueous calcium hydroxide (0.1 M) was completely degraded after 30 min at 100 °C. The principal detected products were 2-hydroxypropanoic acid (lactic acid) and the saccharinic acids, together with their lactones. The same saccharinic acids were produced at all initial concentrations of reactants. Increasing the glucose concentration generally decreased the formation of $<C_6$ acids, hydroxyethanoic acid (glycolic acid, C_2) to hydroxypentanoic acids (deoxypentonic acids, C_5), whereas the C_6 acids (glucosaccharrinic, glucoisosaccharinic and glucometasaccharinic acids) initially increased and then decreased. The C_3 acids, especially 2-hydroxypropanoic (lactic) acid, were found to be the principal components of the reaction products (41%) at lower reaction concentration whereas C_6 acids, such as 2-*C*-methylpentonic (glucosaccharrinic) acids (27%) and the 3-deoxyhexonic (glucometasaccharinic) acids (25%) were found to be major components at higher reactant concentrations. The higher concentrations of glucose appeared to decrease the secondary reactions noted in the more dilute solutions (i.e. diketo-cleavage and aldol condensation). The presence of calcium catalyses the benzilic acid rearrangement, thereby favouring the formation of 3-deoxy-2-*C*-(hydroxymethyl)-pentonic (glucoisosaccharinic) acids, consequently reducing the relative yields of other products, whereas, in the case of sodium hydroxide, considerable fragmentation to 3,4-dihydroxybutanoic (2-deoxytetronic), hydroxyethanoic (glycollic), and methanoic (formic) acids occurs (Machell & Richards, 1960a,b).

3. Alkaline degradation of substituted monosaccharides

The application of the reactions detailed in the Nef–Isbell mechanism to polysaccharides was greatly advanced by the studies of Kenner and co-workers on the alkaline degradation of *O*-substituted derivatives of simple sugars (Corbett, 1959; Corbett, Kenner, & Richards, 1955; Kenner & Richards, 1955, 1957; Richards, 1971). The alkaline degradation of 3-*O*-methyl-D-glucose (**15**) and 4-*O*-methyl-D-glucose (**18**) are

displayed in Figs. 2 and 3, respectively. As in the case for the degradation of glucose, the first stage is the formation of the respective enediols (**16** and **19**) via keto–enol tautomerism (i), which is then followed by enediol deprotonation by hydroxide ions (ii) to produce the corresponding enediol anions (**17** and **20**). In the case of the 3-*O*-methyl-D-glucose degradation pathway (Fig. 2), β-elimination (iv) then occurs. However, in the alkaline degradation of D-glucose, β-hydroxycarbonyl elimination takes place, whereas β-alkoxycarbonyl elimination takes place in the alkaline degradation of 3-*O*-methyl-D-glucose, i.e. the methoxide ion rather than the hydroxide ion is eliminated. Thus, the alkaline degradation of 3-*O*-methyl-D-glucose produces a diketodeoxyglycitol product that is also present in the alkaline degradation of D-glucose (**6**). The degradation pathway then continues as for D-glucose (Fig. 1), i.e. β-alkoxycarbonyl elimination is followed by keto–enol tautomerism (v) and benzilic acid rearrangement (vi), resulting in the formation of a mixture of 3-deoxy-D-arabino-hexonic and 3-deoxy-D-ribo-hexonic acids (D-glucometasaccharinic acids) (**12**) (Fig. 2).

The alkaline degradation of 4-*O*-methyl-D-glucose (Fig. 3) is slightly different. β-alkoxycarbonyl elimination of the enediol anion (**20**) cannot take place straight away since the methoxyl group is not in the β-position relative to the negative charge of the anion, it is in fact in the γ-position. However, after sufficient time has elapsed 4-*O*-methyl-D-fructose is produced via the Lobry de Bruyn/Alberda van Ekenstein transformation (i.e. isomerisation (iii) of anion (**20**) to (**21**) followed by reprotonation). Anion (**21**) has the methoxyl group in the β-position relative to the negative charge of the anion and thus β-alkoxycarbonyl elimination of the enediol anion (**21**) takes place. Therefore, β-alkoxycarbonyl elimination produces a diketodeoxyglycitol product that is also present in the alkaline degradation of D-glucose (**7**). The degradation pathway then continues as for D-glucose (Fig. 1), i.e. keto–enol tautomerism (v) of (**7**) produces 4-deoxy-D-glycero-2,3-hexodiulose (**10**) and subsequent benzilic acid rearrangement (vi) of (**10**) results in the formation of a mixture of 3-deoxy-2-*C*-(hydroxymethyl)-D-threo-pentonic and 3-deoxy-2-*C*-(hydroxymethyl)-D-erythro-pentonic acids (D-glucoisosaccharinic acids) (**13**) (Fig. 3) (Kenner & Richards, 1955).

β-Alkoxycarbonyl elimination occurs more readily than β-hydroxycarbonyl elimination since it is an irreversible reaction whereas all of the others displayed in Figs. 1–3, with the exception of the benzilic acid rearrangement (vi), are reversible and are thus subject to the law of mass action, which inhibits hydroxyl elimination but has no such effect on methoxyl elimination (Kenner & Richards, 1957).

The identity of the saccharinic acids produced upon alkaline degradation can thus be used to provide distinction between 3-*O*- and 4-*O*-substituted sugars (Blears, Machell, & Richards, 1957; Kenner, 1955), and can be applied for studying the alkaline degradation of oligosaccharides and polysaccharides (Burns & Somers, 1973; Whistler & BeMiller, 1958). The formation of 3-deoxy-2-*C*-(hydroxymethyl)-D-erythro- and threo-pentonic acids (D-glucoisosaccharinic acids) is favoured for the alkaline degradation of 4-*O*-substituted glucose derivatives (e.g. 4-*O*-methyl-D-glucose, maltose, amylose and cellulose) with calcium hydroxide, whereas in the case of sodium hydroxide, fragmentation predominates (Machell & Richards, 1960a,b).

4. Cellulose degradation

4.1. End-wise degradation (peeling)

At temperatures $<170\,^{\circ}C$ the glycosidic (1 → 4)-linkages between the β-D-Glc*p* units in cellulose are alkali stable. However, a significant reduction in molecular weight is observed when cellulose is boiled with dilute sodium hydroxide at such temperatures, even with the careful exclusion of oxygen, a problem that was observed many years ago with respect to the scouring of cotton for textile purposes (Fargher & Higginbotham, 1924). Davidson (1934) suggested that the losses were caused by the dissolution of short-chain material detached from the reducing ends of the cellulose molecules (known generally as 'peeling' or 'unzipping'). The predominant mechanism of cellulose degradation was shown to be the formation of the 3-deoxy-2-*C*-(hydroxymethyl)-erythro- and threo-pentonic acids (D-glucoisosaccharinic acids) (**13**) (Colbran & Davidson, 1961; Machell & Richards, 1960a,b; Nevell, 1985a; Richards, 1963; Richards & Sephton, 1957), as in the alkaline degradation of 4-*O*-methyl-D-glucose (Fig. 3). However, in the case of cellulose degradation, β-alkoxycarbonyl elimination (vii) is the elimination of the rest of the cellulose chain to release D-glucoisosaccharinic acids (i.e. the R group in Fig. 3 represents the rest of the β-D-(1 → 4)-

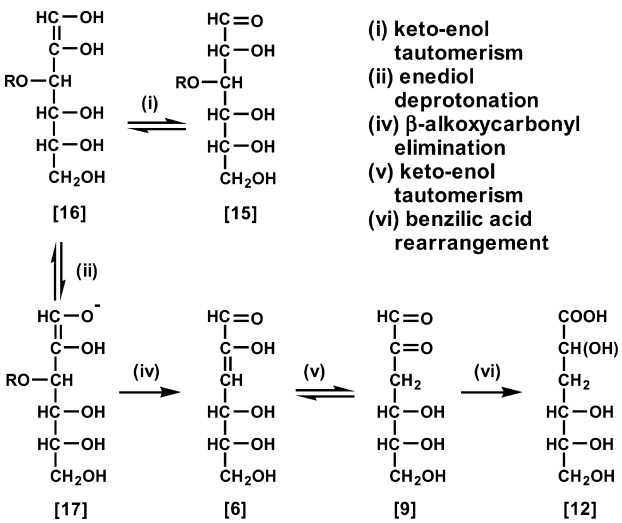


Fig. 2. Alkaline degradation of 3-*O*-substituted D-glucose (**15**).

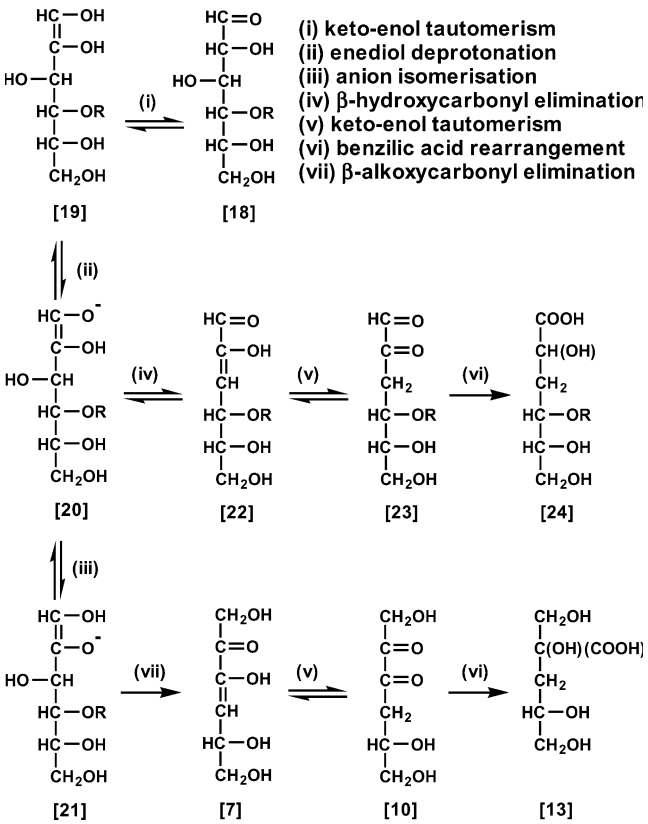


Fig. 3. Alkaline degradation of 4-*O*-substituted D-glucose (**18**).

Glc*p* chain). This generates a new deprotonated end group, which undergoes further alkaline degradation, and so on.

The presence of calcium ions improves the yield of (**13**) by catalysing its production from 4-deoxy-D-glycero-2,3-hexodiulose (**10**). Ziderman (1980) found that alkaline earth metal ions result in a higher weight loss (due to peeling) and consequent greater acid production compared with alkali metal ions, at low alkali concentrations (~0.02 M).

4.2. Termination (stopping)

If the erosion of cellulose molecules from their reducing ends (peeling) were to continue unchecked, the whole of the cellulosic material would eventually dissolve (Nevell, 1985a). However, it is well known that this is not the case, since otherwise the scouring of cotton textiles and the Kraft process for wood pulping would not be possible. Stabilisation of the cellulose is achieved by a competing reaction (a 'stopping' reaction) (Machell & Richards, 1957, 1960b). If one looks at the degradation of a 4-*O*-substituted glucose (Fig. 3), e.g. a cellulose reducing end group, one can see that β-hydroxycarbonyl elimination (iv) can occur. Although, as previously mentioned, β-alkoxycarbonyl elimination (vii) occurs more readily, a significant proportion of β-hydroxycarbonyl elimination (iv) also occurs, resulting in the formation of terminal 4-*O*-substituted 3-deoxy-D-arabino- and ribo-hexonic acid units (**24**), i.e. substituted D-glucometasaccharinic acids (**12**). Besides the 3-deoxyhexonic acid units, 16 other stabilising acid terminal units have been detected in alkali-boiled hydrocellulose (Johansson & Samuelson, 1974, 1975, 1978). The principle behind the stopping reaction can be purposely applied by modifying cellulose end groups in order to produce alkali stable cellulose derivatives (Procter & Wiekenkamp, 1969).

Some reducing end groups can remain in a fully alkali-stabilised hydrocellulose because of their inaccessibility with respect to the alkali (see Section 4.5), due to the physical nature of the cellulosic material (Corbett, 1959, 1960; Haas, Hrutfiord, & Sarkanen, 1967). The concentration of alkali is important with respect to this (Lai & Ontto, 1979). Thus, even with high weight losses due to alkaline hydrolysis (e.g. up to 50%), observed average degree of polymerisation (DP) remains constant (Davidson, 1934) or even increases slightly (Johansson & Samuelson, 1975; Machell & Richards, 1957). Any increase must be due to dissolution of short-chain material in hot alkali.

4.3. Alkaline scission

When cellulose is heated at >170 °C random alkaline scission (hydrolysis) of glycosidic linkages occurs resulting in considerable weight loss and marked decrease in DP (Nevell, 1985a). Scission does not appear to depend on the presence of molecular oxygen and is followed by peeling from any new reducing end group produced by the scission process thereby resulting in much greater weight losses than alkaline degradation at lower temperatures (Richards, 1963, 1971). However, at such higher temperatures end group stabilisation (stopping) has a greater effect than at lower temperatures (Nevell, 1985a).

The glycosidic linkages may be cleaved either between the oxygen atom and the glucosyl group or between the oxygen atom and the aglycone. Both reactions occur, however cleavage of the oxygen–glucosyl bond predominates. A more in depth discussion of the mechanism of alkaline scission can be found in Nevell (1985a). Although alkaline scission is normally only associated with alkaline degradation at higher temperatures, it has been observed in the alkaline degradation of amorphous hydrocellulose at temperatures <100 °C (Gentile, Schroeder, & Atalla, 1987).

4.4. Aerobic (oxidative) alkaline degradation

Although anaerobic conditions will prevail in the long term, there will be a short period of time during and shortly after resaturation when aerobic conditions are present. The oxidation of alkali cellulose by atmospheric molecular oxygen has long been used for the reduction of the DP of wood pulp (the aging or preripening process) to a level suitable for the manufacture of viscose rayon (Treiber, 1985). The first step in this autoxidation process results in the formation of carbonyl-containing oxidised celluloses (oxycelluloses), which are subsequently degraded by alkali

(Klemm et al., 1998; Meller, 1960a,b; Nevell, 1963, 1985b). The reaction is non-specific and may be accompanied by chain scission, but this is not always the case (Richards, 1971). The main functional groups formed are ketone groups but some aldehyde and carboxyl groups are also present (Davidson, 1932; Entwhistle, Cole, & Wooding, 1949).

von Faber and Tollens (1899) made the first significant contribution regarding the chemical reactions involved in the alkaline degradation of oxidised celluloses, finding that oxycelluloses yielded the calcium salt of 3-deoxy-2-*C*-(hydroxymethyl)-pentonic acid (calcium isosaccharinate) as the main degradation product when boiled with lime water, along with small traces of methanoic (formic), 2-hydroxypropanoic (lactic), and 2,3-dihydroxybutanoic (α/β-dihydroxybutyric) acids. The theories of Evans and co-workers (Evans, 1942; Evans & Benoy, 1930; Evans & Hockett, 1931; Gehman et al., 1936) were also applied to explain the breakdown of oxidised celluloses with alkaline solutions (Davidson, 1938, 1940; McGee, Fowler, Unruh, & Kenyon, 1948). A generalised hypothesis for the chemical mechanism of the reactions involved in the alkaline degradation of alkali sensitive oxycelluloses was offered by Pacsu, who identified oxoethanoic (glyoxylic or formylformic) acid as a degradation product (Corbett, 1959).

Haskins and Hogsed (1950) applied the β-alkoxycarbonyl reaction mechanism of Isbell (1944) to the interpretation of the mechanism of reactions between alkali and periodate oxycellulose (i.e. dialdehyde cellulose). Further investigations by O'Meara and Richards (1958a,b) confirmed the application of Isbell's theory to periodate oxycellulose, showing that β-alkoxycarbonyl elimination was the major reaction responsible for its alkaline degradation, with both hydroxyethanoic (glycollic) and 2,4-dihydroxybutanoic (α/γ-dihydroxybutyric) acids found in large proportions among the degradation products. A large number of acids are usually present in the alkaline extract of oxidised celluloses (Haskins & Hogsed, 1950; O'Meara & Richards, 1958a,b; Whistler, Chang, & Richards, 1959a,b). Thus, the alkaline degradation of cellulose and oxycellulose are directly related (Kenner, 1955).

In summary, any resulting oxidised cellulose that contains carbonyl groups at any position other than end groups (i.e. at C2, C3, C6, or combinations thereof) is very alkali labile, and under very mild conditions almost complete scission of the cellulose molecule may be anticipated at any molecule that contains a carbonyl group (Meller, 1960b). Introduction of a carbonyl group to a reducing end group, i.e. conversion to an aldonic acid, has a stabilising effect (Lai, 1991). The alkaline degradation pathways/products of oxidised celluloses have not been fully investigated, although many of the detected degradation products are the same as for the alkaline degradation of cellulose.

4.5. Rate of alkaline degradation

The rate of cellulose degradation is dependent upon the form of the cellulose (Askarieh et al., 2000; Helmy, 1993). In nearly all modes of cellulose degradation the cellulose supramolecular structure (crystallinity or fibrillar morphology) plays a decisive role in determining the rate and often also the course of a degradation process. A high supramolecular order of the polymer chain generally impedes degradation (Klemm et al., 1998). Therefore, amorphous cellulose reacts more readily than crystalline cellulose (Greenfield et al., 1994). The rate-limiting step for slower chemical attack will depend on the rate of mid-chain scission or the reaction of 'inaccessible' end groups (Greenfield et al., 1994). Peeling and chemical stopping are more rapid in amorphous regions compared to crystalline regions. Indeed, Haas et al. (1967) observed that the peeling reaction stops when a molecule is peeled back to a crystalline region. The more ordered physical structure of fibrous hydrocellulose inhibits both peeling and chemical stopping and the majority of partially degraded molecules terminate with inaccessible reducing end groups, i.e. physical stopping (Gentile et al., 1987). The relative rates of degradation (peeling) and stabilisation (stopping) also depend on conditions such as the nature and concentration of the alkali and on temperature. Stabilisation is favoured at high temperature and higher alkali concentrations (Lai & Ontto, 1979).

Significant research has been devoted to investigating the kinetics of the alkaline degradation of (1 → 4)-glucans at low temperatures (Agarwal, McKean, & Gustafson, 1992; Gentile et al., 1987; Haas et al., 1967; Helmy & Elmotagali, 1992; Krochta, Tillin, & Hudson, 1987b; Lai & Sarkanen, 1969; Ziderman & Bel-Ayche, 1978a,b, 1986). At low temperatures, i.e. minimising alkaline scission, such processes can be described in terms of three competing reactions, namely the peeling reaction, the stopping reaction, and termination as a result of complete degradation of a polymer chain. Quantitative depolymerisation occurs at low substrate concentrations, while at raised substrate concentrations an alkali-stable residue is formed, possibly due to intermolecular association between polymer chains (Ziderman & Bel-Ayche, 1978b).

Van Loon and Glaus (1997) presented a model for elucidation of the mechanisms and kinetics of cellulose alkaline degradation, which has been expanded upon by Pavasars (1999). The results of such investigations have been extrapolated in order to perform safety assessment modelling of cellulose-containing waste repositories, i.e. to estimate the extent of cellulose degradation over a suitable timescale. It is predicted that a significant proportion of the cellulose (~15–25%) will be degraded in a relatively short period of time (<5 years). After this time the initial phase of peeling and stopping (both chemical and physical) will be essentially complete, i.e. all accessible chains will have been degraded or stabilised. Therefore, the long-term (i.e.

the very long time scales considered in performance assessment) rate-determining factors for alkaline degradation would be the generation of new accessible reducing end groups via mid-chain alkaline scission of chemically stopped accessible material (or via radiolytic or microbial degradation of any cellulosic material), or the slow reaction of inaccessible end groups. This makes any estimation of the time for complete cellulose degradation very difficult to predict. Alkaline scission is generally thought to occur at a significant rate only at higher temperatures, however as stated previously, Gentile et al. (1987) observed alkaline scission in the degradation of amorphous hydrocellulose at temperatures of <100 °C.

In the absence of measured rate data for either the access of alkali to inaccessible chain ends, and their subsequent reaction, or the rate of mid-chain scission, it is not currently possible to say which single factor, if any, would control the long-term rate of degradation in a repository, i.e. the 'real' situation is likely to be very complex. Indeed, the effects of radiolysis could be the controlling factor in the extent of degradation in the long-term rather than 'pure' chemical reactions. Therefore, when extrapolated over a long time frame (i.e. repository time scales), the slightest variations in the predicted rates of the rate-determining factors discussed above can result in predictions of complete cellulose degradation of anything between one hundred and one million years. Clearly, further investigations using carefully selected model compounds (such as 'stopped' cellulose oligomers) performed over sufficient time frames are required in order to try and exclusively assess alkaline scission rates, i.e. eliminating any peeling effects.

5. Hemicellulose degradation

The chemical composition of wood cannot be defined precisely for a given species or even for a given tree (Pettersen, 1984). However, the major constituents fall into two categories: lignin, which constitutes 18–35% of the dry mass, and carbohydrate (65–75%). The carbohydrate portion is made up of two constituents: cellulose, which accounts for 40–50% of dry wood weight, and hemicellulose (25–35%). Hemicelluloses are mixtures of polysaccharides synthesised in wood almost entirely from glucose, mannose, galactose, xylose, arabinose, 4-*O*-methylglucuronic acid and galacturonic acid residues. They are of much lower molecular weight than cellulose; some are branched and, as they are not crystalline, do not present the same barriers to accessibility as does most of the cellulose. The most significant wood hemicelluloses are the xylans and the β-(1 → 4)-D-glucomannans; hardwoods contain up to 25% of xylans and 5% β-(1 → 4)-D-glucomannans. However, in softwoods the reverse is the case, with β-(1 → 4)-D-glucomannans predominating, and xylans making up only about 10%. The β-(1 → 4)-D-glucomannans consist of a main chain of β-D-glucopyranose and β-D-mannopyranose residues, some of which carry a single residue of β-D-galactopyranose attached to C-6 (Schniewind, 1989). Alkaline degradation of β-(1 → 4)-D-glucomannans would lead to acidic products analogous to those produced from cellulose. Xylan is, like cellulose, a condensation polymer. The basic repeating unit is an anhydroxylopyranose molecule linked by a β-(1 → 4)-bond. The alkaline degradation of xylan leads to the production of the 3-deoxy-2-*C*-(hydroxymethyl)-tetronic acids (xyloisosaccharinic acid) as the major product (Niemelä, Alèn, & Sjöström, 1985). The most significant differences between xylan and cellulose are the presence of branching and the variety of other carbohydrate species as side groups, for example, 4-*O*-methylglucuronic acid. The alkaline pulping of wood therefore results in the formation of numerous acidic by-products, which are receiving more interest with respect to their potential use (Alén, 1990). A detailed account of the chemical degradation of lignocellulosic materials is provided by Lai (1991).

6. Observed cellulose degradation products

A detailed list of the commonly identified alkaline degradation products of glucose, cellobiose and cellulose is presented in Table 1. Alternative nomenclature for detected degradation products is also supplied, where available, since the use of different nomenclature systems between articles, and sometimes in the same article, often results in unnecessary complexity and only serves to cause confusion. The data in Table 1 clearly demonstrates that the majority of these compounds can be detected following the alkaline degradation of cellulose at a wide range of temperatures (20–200 °C), using a range of alkaline degradation agents at different concentrations. The major observed differences due to changes in degradation conditions are the relative concentrations of the observed degradation products. The presence of virtually all of the detected alkaline degradation products can be accounted for by manipulating the degradation mechanisms discussed in Sections 2 and 3 of this review.

Clearly, numerous other products have been detected at trace concentrations, e.g. in the case of the degradation of glucose using calcium hydroxide at 100 °C, Yang and Montgomery (1996) detected >50 components at concentrations of <1%. Up to 65 products were detected by Niemelä and Sjöström (1986) using sodium hydroxide at 170–190 °C, mainly straight-chain and branch-chain hydroxy-monocarboxylic and dicarboxylic acids. Other more unusual degradation products can also be detected at such temperatures (Niemelä, 1987). At higher temperatures ($\sim$280 °C), methanoic (formic), ethanoic (acetic), hydroxyethanoic (glycollic) and 2-hydroxypropanoic (lactic) acids are the major observed degradation products, $\sim$40% based on cellulose starting weight (Krochta, Hudson, & Drake, 1984).

Table 1
Commonly identified alkaline degradation products (Sb = substrate; G = glucose; G_2 = cellobiose; G_n = cellulose; S = sawdust/wood. Alkali: C = $Ca(OH)_2$; K = KOH; N = NaOH; L = lime water. Conc = concentration: M = major (>10%); S = significant (1–10%); T = trace (<1%))

Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
Methanoic acid (formic acid) CH_2O_2	HCOOH	G	C	100	M	Yang and Montgomery (1996)
		G	N	240–320	S	Krochta et al. (1987b)
		G_n	N and L	25	M/S	Machell and Richards (1960a)
		G_n	N/K/C	23	S	Glaus, Van Loon, Achatz, Chodura, and Fischer (1999)
		G_n	N and L	100	M/S	Machell and Richards (1960a) and Richards and Sephton (1957)
		G_n	N	240–320	M	Krochta, Hudson, and Tillin (1987a) and Krochta et al. (1987b)
Ethanoic acid (acetic acid) $C_2H_4O_2$	COOH | CH_3	G	C	100	S	Yang and Montgomery (1996)
		G	N	240–320	S	Krochta et al. (1987b)
		G_n	N/K/C	23	S	Glaus et al. (1999)
		G_n	N	100	S	Richards and Sephton (1957)
		G_n	N	170–190	M	Niemelä and Sjöström (1986)
		G_n	N	240–320	S	Krochta et al. (1987a,b)
Hydroxyethanoic acid (hydroxyacetic acid) (glycollic acid) $C_2H_4O_3$	COOH | CH_2OH	G	C	100	S	Yang and Montgomery (1996)
		G	N	240–320	S	Krochta et al. (1987b)
		G_n	N	20–32	M	Alfredsson and Samuelson (1968), Machell and Richards (1960a), and Shimizu, Kennedy, Lloyd, and Hasamudin (1996)
		G_n	N/K/C	20–60	S	Bourbon and Toulhoat (1996) and Glaus et al. (1999)
		G_n	N	96–100	S	Machell and Richards (1960a) and Richards and Sephton (1957)
		G_n	N	170–190	S	Johansson and Samuelson (1978) and Niemelä and Sjöström (1986)
		G_n	N	240–320	S	Krochta et al. (1987a,b)
2-Hydroxy-propanoic acid (2-hydroxy-propionic acid) (DL-lactic acid) (3-deoxy-DL-glyceric acid) $C_3H_6O_3$	COOH | CH(OH) | CH_3	G	N	25 and 45	M	MacLeod and Schroeder (1982)
		G	C	100	M	Yang and Montgomery (1996)
		G_2	N	25 and 45	M	MacLeod and Schroeder (1982)
		G_n	C and N	20–32	S	Alfredsson and Samuelson (1968) and Shimizu et al. (1996)
		G_n	N/K/C	20–60	S	Bourbon and Toulhoat (1996) and Glaus et al. (1999)
		G_n	N and L	100	S	Machell and Richards (1960a) and Richards and Sephton (1957)
		G_n	N	170–190	M/S	Johansson and Samuelson (1978) and Niemelä and Sjöström (1986)
		G_n	N	240–320	M	Krochta et al. (1987a,b)
2,3-Dihydroxypropanoic acid (DL-glyceric acid) (3-hydroxy-DL-lactic acid) $C_3H_6O_4$	COOH | CH(OH) | CH_2OH	G	N	25 and 45	S	MacLeod and Schroeder (1982)
		G	C	100	S	Yang and Montgomery (1996)
		G_2	N	25 and 45	S	MacLeod and Schroeder (1982)
		G_n	N/K/C	19–23	S	Glaus et al. (1999) and Pavasars (1999)
		G_n	N	96 and 170	S	Johansson and Samuelson (1978)
Butanedioic acid (succinic acid) $C_4H_6O_4$	COOH | $(CH_2)_2$ | COOH	S	N/K/C	19–60	T	Bourbon and Toulhoat (1996), Glaus et al. (1999) and Pavasars (1999)

(*continued on next page*)

Table 1 (*continued*)

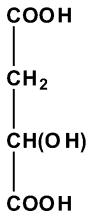
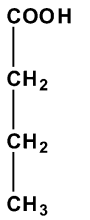
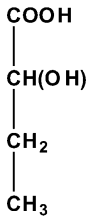
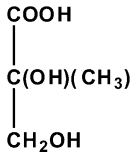
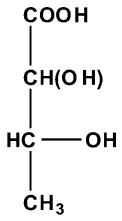
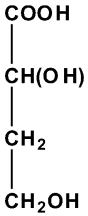
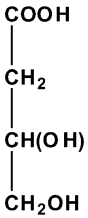
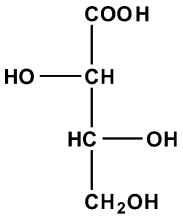
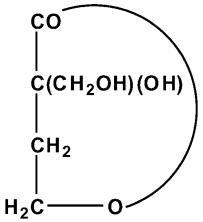
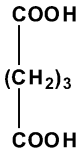
Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
Hydroxybutanedioic acid (DL-hydroxysuccinic acid) (DL-malic acid) $C_4H_6O_5$		G_n	N/K/C	19–23	T	Pavasars (1999)
Butanoic acid (butyric acid) (2,3,4-trideoxytetronic acid) $C_4H_8O_2$		G_n G_n	N/K/C N	23 240–300	S S	Glaus et al. (1999) Krochta et al. (1987a,b)
2-Hydroxybutanoic acid (3,4-dideoxytetronic acids) $C_4H_8O_3$		G_n G_n	N/K/C N	20–60 240–320	– S	Bourbon and Toulhoat (1996) Krochta et al. (1987a,b)
2-Methyl-2,3-dihydroxypropanoic acid (2-methyl-DL-glyceric acid) (2-methyl-3-hydroxy-DL-lactic acid) $C_4H_8O_4$		G G_n G_n G_n	C N/K/C N N	100 19–23 95–100 170	S T M M	Yang and Montgomery (1996) Pavasars (1999) Johansson and Samuelson (1975, 1978) and Richards and Sephton (1957) Johansson and Samuelson (1978)
2,3*R*-dihydroxybutanoic acid (4-deoxy-D-erythro- and D-threo-tetronic acids) $C_4H_8O_4$		S G_n	N/K/C N	19–23 100	T –	Pavasars (1999) Richards and Sephton (1957)

Table 1 (*continued*)

Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
2,4-Dihydroxy-butanoic acid (3-deoxytetronic acids) $C_4H_8O_4$		G	N	25 and 45	M	MacLeod and Schroeder (1982)
		G	C	100	S	Yang and Montgomery (1996)
		G_2	N	25 and 45	M	MacLeod and Schroeder (1982)
		G_n	N/K/C	19–23	T	Pavasars (1999)
		G_n	N	20–32	S	Alfredsson and Samuelson (1968) and Shimizu et al. (1996)
		G_n	N	170–190	S	Niemelä and Sjöström (1986)
3,4-Dihydroxybutanoic acid (2-deoxy-DL-tetronic acids) $C_4H_8O_4$		G_n	N/K/C	19–60	S	Bourbon and Toulhoat (1996) and Pavasars (1999)
		G_n	C and N	20–32	S	Alfredsson and Samuelson (1968) and Shimizu et al. (1996)
2*S*,3*R*,4-Trihydroxybutanoic acid (D-threo-tetronic acid) (D-threonic acid) $C_4H_8O_5$		G_n	N/K/C	23	S	Glaus et al. (1999)
		G_n	N	95	S/T	Johansson and Samuelson (1975, 1978)
2-Hydroxy-2-hydroxymethyl-4-hydroxybutanoic acid-1,4-lactone (3-deoxy-2-*C*-(hydroxymethyl)-tetrono-1,4-lactone) (D-xyloisosaccharino-1,4-lactone) $C_5H_8O_4$		G_n	N/K/C	19–23	S	Pavasars (1999)
Pentanedioic acid $C_5H_8O_4$		S	N/K/C	19–23	T	Pavasars (1999)

(*continued on next page*)

Table 1 (*continued*)

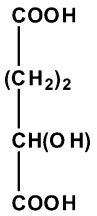
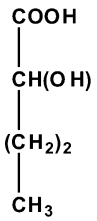
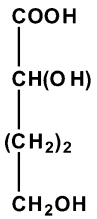
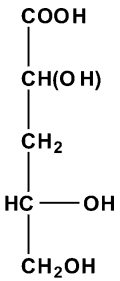
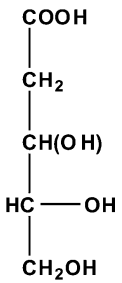
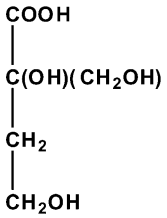
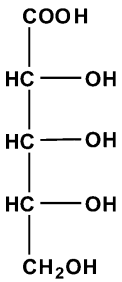
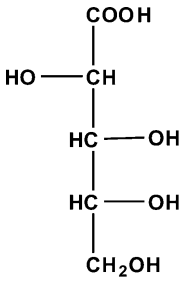
Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
2-Hydroxypentanedioic acid $C_5H_8O_5$		G_n	N/K/C	19–23	S	Pavasars (1999)
2-Hydroxypentanoic acid (2-hydroxyvaleric acid) (3,4,5-trideoxypentonic acids) $C_5H_{10}O_3$		G_n	N	240–300	S	Krochta et al. (1987a,b)
2,5-Dihydroxypentanoic acid (3,4-dideoxypentonic acids) $C_5H_{10}O_4$		G	C	100	S	Yang and Montgomery (1996)
		G_2	N	25 and 45	S	MacLeod and Schroeder (1982)
		G_n	N	32	S	Alfredsson and Samuelson (1968)
		G_n	N/K/C	20–60	–	Bourbon and Toulhoat (1996)
		G_n	N	170–190	S	Niemelä and Sjöström (1986)
2,4*R*,5-Trihydroxypentanoic acid (3-deoxy-D-pentonic acids) (3-deoxy-D-erythro- and D-threo-pentonic acids) $C_5H_{10}O_5$		G	N	25 and 45	S	MacLeod and Schroeder (1982)
		G	C	100	T	Yang and Montgomery (1996)
		G_2	N	25 and 45	S	MacLeod and Schroeder (1982)
		G_n	C and N	20–32	S	Alfredsson and Samuelson (1968) and Shimizu et al. (1996)
		G_n	N/K/C	20–60	–	Bourbon and Toulhoat (1996)

Table 1 (*continued*)

Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
3,4*R*,5-Trihydroxypentanoic acid) (2-deoxy-D-erythro- and D-threo-pentonic acids) $C_5H_{10}O_5$		G_n G_n	C N	20–30 95	– S	Shimizu et al. (1996) Johansson and Samuelson (1975, 1978)
2-Hydroxymethyl-2,4-dihydroxybutanoic acid (2-*C*-(hydroxymethyl)-3-deoxytetronic acids) (xyloisosaccharinic acid) $C_5H_{10}O_5$		G_n	N/K/C	19–23	S	Pavasars (1999)
2*R*,3*R*,4*R*,5-Tetrahydroxypentanoic acid (D-ribonic acid) (D-ribo-pentonic acid) $C_5H_{10}O_6$		G_n	N	95	T	Johansson and Samuelson (1975, 1978)
2*S*,3*R*,4*R*,5-Tetrahydroxypentanoic acid (D-arabinonic acid) (D-arabino-pentonic acid) $C_5H_{10}O_6$		G_n	N	95 and 170	S	Johansson and Samuelson (1975, 1978)

(*continued on next page*)

Table 1 (*continued*)

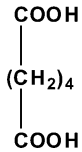
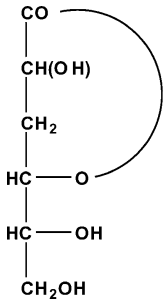
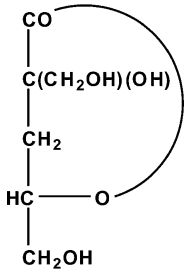
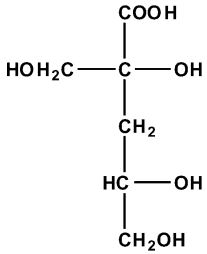
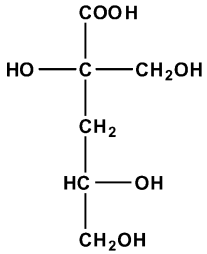
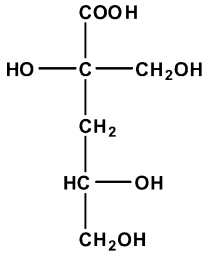
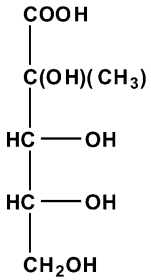
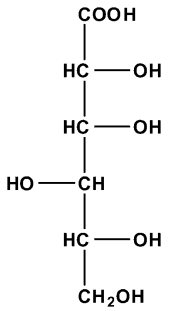
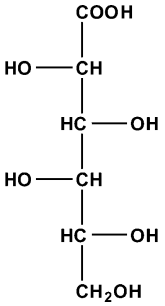
Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
Hexanedioic acid (adipic acid) $C_6H_{10}O_4$		G_n	N/K/C	23	T	Glaus et al. (1999)
2,4*R*,5*R*,6-Tetra-hydroxyhexanoic acid-1,4-lactone (3-deoxy-D-arabino- and D-ribo-hexono-1,4-lactone) (D-glucometasaccharino-1,4-lactone) $C_6H_{10}O_5$		G	C	100	T	Yang and Montgomery (1996)
		G_n	N	20–30	–	Shimizu et al. (1996)
		G_n	N/K/C	20–60	–	Bourbon and Toulhoat (1996)
2-Hydroxymethyl-2,4,5-trihydroxypentanoic acid-1,4-lactone (3-deoxy-2-*C*-(hydroxymethyl)-D-erythro- and D-threo-pentono-1,4-lactone) (D-glucoisosaccharino-1,4-lactone) $C_6H_{10}O_5$		G_n	N/K/C	19–23	M	Pavasars (1999)
		G_n	N/K/C	23	M	Glaus et al. (1999)
		G_n	N/K/C	20–60	–	Bourbon and Toulhoat (1996)
		G_n	N	100	–	Richards and Sephton (1957)
		G_n	N	170–190	S	Niemelä and Sjöström (1986)
2*S*,4*R*,5-Trihydroxy-2*S*-hydroxymethylpentanoic acid (3-deoxy-2-*C*-(hydroxymethyl)-D-erythro-pentonic acid) (α-D-glucoisosaccharinic acid) $C_6H_{12}O_6$		G	C	100	S	Yang and Montgomery (1996)
		G_2	N	25 and 45	M	MacLeod and Schroeder (1982)
		G_n	N/K/C	19–60	M	Bourbon and Toulhoat (1996), Glaus et al. (1999), and Pavasars (1999)
		G_n	C and N	20–32	M	Alfredsson and Samuelson (1968) and Shimizu et al. (1996)
		G_n	N and L	25	M	Machell and Richards (1960a)
		G_n	N and L	100	M	Machell and Richards (1960a) and Richards and Sephton (1957)
		G_n	N	170–190	S	Niemelä and Sjöström (1986)

Table 1 (*continued*)

Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
2*R*,4*R*,5-Trihydroxy-2*S*-hydroxymethylpentanoic acid (3-deoxy-2-*C*-(hydroxymethyl)-D-threo-pentonic acid) (β-D-glucoisosaccharinic acid) $C_6H_{12}O_6$		G_n G_n G_n G_n G_n	N/K/C N and C L N and L N	19–23 20–30 25 100 170–190	M M M M M	Glaus et al. (1999) and Pavasars (1999) Alfredsson and Samuelson (1968) and Shimizu et al. (1996) Machell and Richards (1960a) Machell and Richards (1960a) and Richards and Sephton (1957) Niemelä and Sjöström (1986)
(2,4*R*,5*R*,6-tetrahydroxyhexanoic acid) (3-deoxy-D-ribo- and 3-deoxy-D-arabino-hexonic acids) (3-deoxy-D-gluconic and D-mannonic acid) (D-glucometasaccharinic acid) $C_6H_{12}O_6$		G_n G_n G_n	C and N N/K/C N	20–45 20–60 95–100	M/S – M	Alfredsson and Samuelson (1968), MacLeod and Schroeder (1982), and Shimizu et al. (1996) Bourbon and Toulhoat (1996) Johansson and Samuelson (1975, 1978), Richards and Sephton (1957), and Yang and Montgomery (1996)
2-Methyl-2,3,4,5-tetrahydroxypentanoic acid (2-*C*-methyl-D-ribonic and D-arabinonic acid) (2-*C*-methyl-D-ribo- and D-arabino-pentonic acid) (glucosaccharinic acid) $C_6H_{12}O_6$		G_n G_n	N N/K/C	95 and 170 19–23	T T	Johansson and Samuelson (1975, 1978) Pavasars (1999)
2*R*,3*R*,4*S*,5*R*,6-pentahydroxyhexanoic acid (D-gluconic acid) $C_6H_{12}O_7$		G_n	N	95 and 170	S	Johansson and Samuelson (1975, 1978)

(*continued on next page*)

Table 1 (*continued*)

Component name(s)	Structure	Sb	Alkali	Temp. (°C)	Conc	Reference(s)
2*S*,3*R*,4*S*,5*R*,6-penta-hydroxyhexanoic acid (D-mannonic acid) $C_6H_{12}O_7$		G_n	N	95 and 170	T	Johansson and Samuelson (1975, 1978)

At lower temperatures the glucoisosaccharinic acids (α and β forms) and their lactones are undoubtedly the major observed alkaline degradation products. Glucoisosaccharinic acid comprised ~70 and 85% of cellulose degradation products at cellulose-to-water ratios of 5 and 100 g/l, respectively (Pavasars, 1999).

It is interesting to note the effect of calcium/magnesium hydroxide on the alkaline degradation of glucose. The same degradation compounds were detected as in the case of using only calcium hydroxide, however glucometasaccharinic acid was a more significant component (i.e. the stopping reaction increased) and total amount of acids produced significantly decreased (~40% on a molar basis) (Yang & Montgomery, 1996).

7. Conclusions

The degradation of cellulose under alkaline conditions has been reviewed focusing on its relevance to the possible disposal of radioactive wastes in an underground repository in which cement-based waste encapsulation grouts and backfill may be employed. A multitude of degradation products have been detected by researchers investigating this area over the last 50 years (the commonly detected products being listed in Table 1), and the majority of the mechanisms of the degradation pathways resulting in their formation have been elucidated. The onset of cellulose degradation occurs at a relatively rapid rate. The initial degradation rate is governed by the peeling mechanism and depends on the concentration of reducing end groups (which is approximately equal to the reciprocal of the DP). Later as the degradation continues, alkaline hydrolysis of glycosidic linkages becomes the rate-limiting mechanism, and is not dependent on DP.

The calcium present in the cement catalyses the benzilic acid rearrangement favouring the production of glucoisosaccharinic acids, and the relatively low temperature also favours formation of glucoisosaccharinic acids, making them the major degradation products in an alkaline repository environment. Clearly, many other degradation products would also be present at varying concentrations.

In conclusion, many organic species will be generated in a repository as a function of the alkaline degradation of cellulose with time. Clearly the relative concentration of such potential complexants depends upon the storage conditions within the repository, namely temperature, alkali concentration, cellulose concentration, etc. all of which will have an effect upon the overall rate of cellulose degradation.

Acknowledgments

This review was carried out under contract to AEA Technology as part of the Nirex Safety Assessment Research Programme (NSARP). The authors would like to express their gratitude to Dr N. J. Pilkington and Dr S. J. Williams of AEA Technology, Nuclear Science, 220 Harwell, Didcot, Oxfordshire, OX11 0QJ, UK for their guidance on the scope of the review.

References

Agarwal, N., McKean, W. T., & Gustafson, R. R. (1992). Cellulose degradation kinetics in alkaline pulping. *Appita Journal*, *45*(3), 165–169.

Agg, P. J., Cummings, R. W., Rees, J. H., Rodwell, W. R., & Wikramaratna, R (1996). Nirex gas generation and migration research: Report on current status in 1994. *Nirex Science Report*, S/96/002.

Alén, R. (1990). Conversion of cellulose-containing materials into useful products. In J. F. Kennedy, G. O. Phillips, & P. A. Williams (Eds.), *Cellulose sources and exploitation* (pp. 453–464). Chichester: Ellis Horwood.

Alfredsson, B., & Samuelson, O. (1968). Hydroxy acids formed by alkali treatment of hydrocellulose. *Svensk Papperstidning*, *71*(19), 679–686.

Arter, H. E., Hanselmann, K. W., & Bachofen, R. (1991). Modelling of microbial degradation processes: The behaviour of microorganisms in a waste repository. *Experientia*, *47*(6), 578–583.

Arthur, J. C. (1958). The effects of gamma radiation on cotton, part II: Proposed mechanism of the effects of high energy gamma radiation on some of the molecular properties of purified cotton. *Textile Research Journal*, *28*, 204–206.

Arthur, J. C. (1971). Reactions induced by high energy radiation. In N. M. Bikales, & L. Segal (Eds.), *High polymers, volume V: Cellulose and cellulose derivatives* (pp. 937–975). Chichester: Wiley.

Askarieh, M. M., Chambers, A. V., Daniel, F. B. D., FitzGerald, P. L., Holtom, G. J., Pilkington, N. J., & Rees, J. H. (2000). The chemical and microbial degradation of cellulose in the near field of a repository for radioactive wastes. *Waste Management*, *20*(1), 93–106.

Askarieh, M. M., Chambers, A. V., Hickford, G. E., & Sharland, S. M. (1998). The role of engineered barriers in the performance assessment of a repository for L/ILW. In I. G. McKinley, & C. McCombie (Eds.), *Scientific basis for nuclear waste management XXI* (*Vol. 506*) (pp. 465–476). *Materials Research Society Symposium Series*, Pittsburgh: Materials Research Society.

Askarieh, M. M., & Worth, S. V. (1999). Post-closure thermal evolution of a conceptual repository design for the disposal of intermediate-level radioactive waste. *Commitment to the future environment* (*Vol. II*). *Proceedings of ENS Topseal'99 Meeting*, Belgian Nuclear Society.

Atkins, N., & Glasser, F. P. (1992). Application of portland cement-based materials to radioactive waste immobilisation. *Waste Management*, *12*(2/3), 105–131.

Bachofen, R. (1991). Microorganisms in nuclear waste disposal: Conclusions. *Experientia*, *47*(6), 583–584.

Baker, A. J., Chambers, A. V., Jackson, C. P., Porter, J. D., Sinclair, J. E., Sumner, P. J., Thorne, M. C., & Watson, S. P (1997). Nirex 97: An assessment of the post-closure performance of a deep waste repository at Sellafield. The groundwater pathway (Vol. 3). *Nirex Sience Report*, S/97/012.

Baston, G. M. N., Berry, J. A., Bond, K. A., Brownsword, M., & Linklater, C. M. (1992). Effects of organic degradation products on the sorption of actinides. *Radiochimica Acta*, *58/59*, 349–356.

Bellamy, W. D., & Miller, A. A. (1963). The effect of ionising radiation on cellulose and its derivatives. In R. L. Whistler (Ed.), *Methods in carbohydrate chemistry* (*Vol. III*) (pp. 185–189). *Cellulose*, New York: Academic Press.

Biddle, P., Greenfield, B. F., Pilkington, N. J., & Spindler, M. W (2000). Further studies on the effects of the products from the anaerobic degradation of cellulosic wastes in the near field. *AEA Technology Report*, AEAT/ERRA-0154.

Blazej, A., & Kosik, M. (1985). Degradation reactions of cellulose and lignocellulose. In J. F. Kennedy, G. O. Phillips, & P. A. Williams (Eds.), *Cellulose and its derivatives: Chemistry, biochemistry and applications* (pp. 97–117). Chichester: Ellis Horwood.

Blazej, A., Kosik, M., & Spilda, I. (1990). The degradation of cellulose by thermal, chemical and biochemical techniques. In J. F. Kennedy, G. O. Phillips, & P. A. Williams (Eds.), *Cellulose sources and exploitation* (pp. 385–396). Chichester: Ellis Horwood.

Blears, M. J., Machell, G., & Richards, G. N. (1957). Alkaline degradation of 4-*O*-substituted glucose derivatives. *Chemical & Industry (London)*, 1150–1151.

Blouin, F. A., & Arthur, J. C. (1958). The effects of gamma radiation on cotton, part I: Some of the properties of purified cotton irradiated in oxygen and nitrogen atmospheres. *Textile Research Journal*, *28*, 198–204.

Bourbon, X., & Toulhoat, P. (1996). Influence of organic degradation products on the solubilisation of radionuclides in intermediate and low level radioactive wastes. *Radiochimica Acta*, *74*, 315–319.

Bradshaw, S., Gaudie, S. C., Greenfield, B. F., Long, S., Spindler, M. W., & Wilkins, J. D (1987). Experimental studies on the chemical and radiation decomposition of intermediate level wastes containing organic materials. *UKAEA Report*, AERE-R.12806.

Bradshaw, S., Gaudie, S. C., Greenfield, B. F., Lyon, C. E., Rees, J. H., Spindler, M. W., & Wilkins, J. D (1986). Preliminary experimental studies on the chemical and radiation degradation of combustible plutonium contaminated material. *UKAEA Report*, AERE-R.12223.

de Bruijn, J. M., Kieboom, A. P. G., & van Bekkum, H. (1986). Alkaline-degradation of monosaccharides, 3: Influence of reaction parameters upon the final product composition. *Recueil des Travaux Chimiques du Pays-Bas*, *105*(6), 176–183.

de Bruijn, J. M., Kieboom, A. P. G., & van Bekkum, H. (1987a). Alkaline-degradation of monosaccharides, 7: A mechanistic picture. *Starch-Stärke*, *39*(1S), 23–28.

de Bruijn, J. M., Kieboom, A. P. G., & van Bekkum, H. (1987b). Alkaline-degradation of monosaccharides, 5: Kinetics of the alkaline isomerisation and degradation of monosaccharides. *Recueil des Travaux Chimiques du Pays-Bas*, *106*(2), 35–43.

Burns, R. F., & Somers, P. J. (1973). Linkage analysis of (1 → 6)-linked oligosaccharides by alkaline degradation. *Carbohydrate Research*, *31*, 191–197.

Chambers, A. V., Williams, S. J., & Wisbey, S. J (1995). Nirex near field research: Report on current status in 1994. *Nirex Science Report*, S/95/011.

Christofi, N., & Philp, J. C. (1991). Microbiology of subterranean waste sites. *Experientia*, *47*(6), 524–527.

Colbran, R. L., & Davidson, G. F. (1961). The degradative action of hot dilute alkalis on hydrocellulose. *Journal of Textile Institute*, *52*, T73–T87.

Corbett, W. M. (1959). The alkaline degradation of cellulose and chemically modified cellulose. In J. Honeyman (Ed.), *Recent advances in the chemistry of cellulose and starch* (pp. 106–133). London: Heywood.

Corbett, W. M. (1960). The alkaline degradation of chemically modified cellulose. *Journal of the Society of Dyers Colourists*, *76*, 265–271.

Corbett, W. M., Kenner, J., & Richards, G. N. (1955). The degradation of carbohydrates by alkali, part X: Acetal derivatives. *Journal of Chemical Society*, 1709–1711.

Coutts, D. A. P., Grant, W. D., O'Kelly, N., Pugh, S. Y. R., Malpass, J. R., Rosevear, A., Walter, E. R., & Widdowson, D (1997). Microbiological research in support of the Nirex Near-field chemistry programme. *Nirex Report*, NSS/R328.

David, C., & Van den Bergh, M. A. (1982). Utilisation of waste cellulose, II: Gamma irradiation and alkaline hydrolysis. *Cellulose Chemistry & Technology*, *16*, 153–158.

Davidson, G. F. (1932). The oxidation by gaseous oxygen of cotton impregnated with sodium hydroxide solution. *Journal of Textile Institute*, *23*, T95–T133.

Davidson, G. F. (1934). The solution of chemically modified cotton cellulose in alkaline solutions, I: In solutions of sodium hydroxide particularly at temperatures below the normal. *Journal of Textile Institute*, *25*, T174–T196.

Davidson, G. F. (1938). The effect of alkalis on the molecular chain length of chemically modified cotton celluloses, as shown by fluidity measurements on the derived nitrocelluloses. *Journal of Textile Institute*, *29*(9), T195–T218.

Davidson, G. F. (1940). Properties of the oxycelluloses formed in the early stages of the oxidation of cotton cellulose by periodic acid and metaperiodate. *Journal of Textile Institute*, *31*(7), T81–T96.

DEFRA (Department for Environment, Food and Rural Affairs) (2001). Managing radioactive waste safely, proposals for developing a policy for managing solid radioactive waste in the UK.

Entwhistle, D., Cole, E. H., & Wooding, N. S. (1949). The autoxidation of alkali cellulose, I: An experimental study of the kinetics of the reaction. *Textile Research Journal*, *19*, 527–546.

Evans, W. L. (1942). Some less familiar aspects of carbohydrate chemistry. *Chemical Review*, *31*, 537–560.

Evans, W. L., & Benoy, M. P. (1930). The mechanism of carbohydrate oxidation, XI: The action of potassium hydroxide on maltose. *Journal of American Chemical Society*, *52*, 294–307.

Evans, W. L., & Hockett, R. C. (1931). The mechanism of carbohydrate oxidation, XIV: The alkaline degradation of cellobiose, lactose, melibiose and gentiobiose by potassium hydroxide. *Journal of American Chemical Society*, *53*, 4384–4400.

von Faber, O., & Tollens, B. (1899). Untersuchungen über die oxycellulose. *Berichte der Deutschen Chemischen Gesellschaft*, *32*, 2589–2601.

Fargher, R. G., & Higginbotham, L. (1924). Chemical analysis of cotton: Micro-analytical methods for the examination of small quantities of waxes, in particular cotton wax. *Journal of Textile Institute*, *15*, T75–T80.

Forsskåhl, I., Popoff, T., & Theander, O. (1976). Reactions of D-xylose and D-glucose in alkaline aqueous solutions. *Carbohydrate Research*, *48*, 13–21.

Francis, A. J., Cather, R., & Crossland, I. G. (1997). Development of the Nirex Reference Vault Backfill. Report on current status in 1994. *Nirex Science Report*, S/97/014.

Gehman, H., Kreider, L. C., & Evans, W. L. (1936). The mechanism of carbohydrate oxidation, XXIII: A contribution to the alkaline hydrolysis of oligosaccharides. *Journal of American Chemical Society*, *58*, 2388–2395.

Gentile, V. M., Schroeder, L. R., & Atalla, R. H. (1987). Physical structure and alkaline degradation of hydrocellulose. In R. H. Atalla (Ed.), *The structures of cellulose—Characterisation of the solid states* (pp. 272–291). *ACS Symposium Series 340*, Washington: American Chemical Society.

Glaus, M. A., Van Loon, L. R., Achatz, S., Chodura, A., & Fischer, K. (1999). Degradation of cellulosic materials under the alkaline conditions of a cementitious repository for low and intermediate level radioactive waste, part 1: Identification of degradation products. *Analytica Chimica Acta*, *398*, 111–122.

Grant, W. D., Holtom, G. J., Rosevear, A., & Widdowson, D. (1997). A review of environmental microbiology relevant to the disposal of radioactive waste in a deep underground repository. *Nirex Report*, NSS/R329.

Greenfield, B. F., Harrison, W. N., Robertson, G. P., Somers, P. J., & Spindler, M. W. (1993). Mechanistic studies of the alkaline degradation of cellulose in cement. *Nirex Report*, NSS/R272.

Greenfield, B. F., Hurdus, M. H., Pilkington, N. J., Spindler, M. W., & Williams, S. J. (1994). The degradation of cellulose in the near field of a radioactive waste repository. In A. Barkatt, & R. A. Konynenburg (Eds.), *Scientific basis for nuclear waste management XVII* (*Vol. 333*) (pp. 705–710). *Materials Research Society Symposium Series*, Pittsburgh: Materials Research Society.

Greenfield, B. F., Hurdus, M. H., Spindler, M. W., & Thomason, H. P. (1997). The effects of the products from the anaerobic degradation of

cellulose on the solubility and sorption of radioelements in the near field. *Nirex Report*, NSS/R376.

Greenfield, B. F., Holtom, G. J., Hurdus, M. H., O'Kelly, N., Pilkington, N. J., Rosevear, A., Spindler, M. W., & Williams, S. J. (1995). The identification and degradation of isosaccharinic acid, a cellulose degradation product. In T. Murakami, & R. C. Ewing (Eds.), *Scientific bases for nuclear waste management XVIII* (*Vol. 353*) (pp. 1151–1158). *Materials Research Society Symposium Series*, Pittsburgh: Materials Research Society.

Greenfield, B. F., Rosevear, A., & Williams, S. J. (1990). Review of the microbiological, chemical and radiolytic degradation of organic material likely to be present in intermediate level and low level radioactive wastes. *UK DoE Report*, DOE/HMIP/RR/91/002.

Haas, D. W., Hrutfiord, B. F., & Sarkanen, K. V. (1967). Kinetic study on the alkaline degradation of cotton hydrocellulose. *Journal of Applied Polymer Science*, *11*, 587–600.

Harrison, W. N. (1991). *The effects of cellulose degradation on waste plutonium solubility*. PhD thesis, University of Birmingham, UK.

Haskins, J. F., & Hogsed, M. J. (1950). The alkaline oxidation of cellulose, I: Mechanism of the degradative oxidation of cellulose by hydrogen peroxide in presence of alkali. *Journal of Organic Chemistry*, *15*, 1264–1274.

Helmy, S. A. (1993). Studies on the alkaline degradation of cellulose 2, effect of the supermolecular structure of the pulp. *Polymer Degradation Stability*, *39*(2), 159–162.

Helmy, S. A., & Elmotagali, H. A. A. (1992). Studies on the alkaline degradation of cellulose, 1: Changes in the characteristics of cellulose with time and temperature. *Polymer Degradation & Stability*, *38*(3), 235–238.

Ilett, D. J., Pilkington, N. J., & Tweed, C. J. (1998). Complexation of radionuclides. Proceedings of the Royal Society of Chemistry/Nirex Symposium: The chemistry of deep disposal of radioactive waste. *Nirex Science Report*, S/98/008.

Isbell, H. S. (1944). Interpretation of some reactions in the carbohydrate field in terms of consecutive electron displacement. *Journal of Research National Bureau of Standards*, *32*, 45–59.

Johansson, M. H., & Samuelson, O. (1974). The formation of end groups in cellulose during alkali cooking. *Carbohydrate Research*, *34*, 33–43.

Johansson, M. H., & Samuelson, O. (1975). Endwise degradation of hydrocellulose during hot alkali treatment. *Journal of Applied Polymer Science*, *19*, 3007–3013.

Johansson, M. H., & Samuelson, O. (1978). Endwise degradation of hydrocellulose in bicarbonate solution. *Journal of Applied Polymer Science*, *22*, 615–623.

Kenner, J. (1955). The alkaline degradation of carbonyl oxycelluloses and the significance of saccharic acids for the chemistry of carbohydrates. *Chemistry & Industry (London)*, 727–730.

Kenner, J., & Richards, G. N. (1955). The degradation of carbohydrates by alkali, part XI: 4-*O*-methyl derivatives of glucose and fructose. *Journal of Chemical Society*, 1810–1813.

Kenner, J., & Richards, G. N. (1957). The degradation of carbohydrates by alkali, part XV: Factors in the formation of metasaccharinic acids from 3-*O*-derivatives of glucose. *Journal of Chemical Society*, 3019–3024.

Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). Degradation of cellulose. *Comprehensive cellulose chemistry* (*Vol. 1*). *Fundamentals and analytical methods*, Weinheim: Wiley, pp. 83–129.

Krochta, J. M., Hudson, J. S., & Drake, C. W. (1984). Alkaline thermochemical degradation of cellulose to organic acids. *Biotechnology and Bioengineering*, *S14*, 37–54.

Krochta, J. M., Hudson, J. S., & Tillin, S. J. (1987a). Kinetics of alkaline thermochemical degradation of polysaccharides to organic acids. *American Chemical Society Division of Fuel Chemistry*, *32*, 148–156.

Krochta, J. M., Tillin, S. J., & Hudson, J. S. (1987b). Degradation of polysaccharides in alkaline solution to organic acids: Product characterisation and identification. *Journal of Applied Polymer Science*, *33*, 1413–1425.

Lai, Y.-Z. (1991). Chemical degradation. In D. N.-S. Hon, & N. Shiraishi (Eds.), *Wood and cellulosic chemistry* (pp. 455–523). New York: Marcel Dekker.

Lai, Y.-Z., & Ontto, D. E. (1979). Effects of alkalinity on endwise depolymerization of hydrocellulose. *Journal of Applied Polymer Science*, *23*, 3219–3225.

Lai, Y.-Z., & Sarkanen, K. V. (1969). Kinetic study on the alkaline degradation of amylose. *Journal of Polymer Science, Part C*, *28*, 15–26.

Lobry de Bruyn, C. A., & Alberda van Ekenstein, W. (1895a). Action des alcalis sur les sucres II: Transformation réciproque des uns dans les autres des sucres, glucose, fructose et mannose. *Recueil des Travaux Chimiques du Pays-Bas*, *14*, 203–216.

Lobry de Bruyn, C. A., & Alberda van Ekenstein, W. (1895b). Einwirkung von Alkalien auf Kohlehydrate: Wechselseitige Umwandlung von Glucose, Fructose und Mannose in einander. *Berichte der Deutschen Chemischen Gesellschaft*, *28*, 3078–3082.

Lobry de Bruyn, C. A., & Alberda van Ekenstein, W. (1897). Action des alcalis sur les sucres IV: Remarques générales. *Recueil des Travaux Chimiques du Pays-Bas*, *16*, 257–261.

Machell, G., & Richards, G. N. (1957). The alkaline degradation of polysaccharides, part II: The alkali-stable residue from the action of sodium hydroxide on cellulose. *Journal of Chemical Society*, 4500–4506.

Machell, G., & Richards, G. N. (1960a). Mechanism of saccharinic acid formation, part I: Competing reactions in the alkaline degradation of 4-*O*-methyl-D-glucose, maltose, amylose and cellulose. *Journal of Chemical Society*, 1924–1931.

Machell, G., & Richards, G. N. (1960b). Mechanism of saccharinic acid formation, part II: The α/β-dicarbonyl intermediate on formation of D-glucoisosaccharinic acid. *Journal of Chemical Society*, 1932–1938.

Machell, G., & Richards, G. N. (1960c). Mechanism of saccharinic acid formation, part III: The α-keto-aldehyde intermediate in formation of D-glucometasaccharinic acid. *Journal of Chemical Society*, 1938–1944.

MacLeod, J. M., & Schroeder, L. R. (1982). Alkaline degradation of cellobiose, 3,6-anhydro4-*O*-(β-D-glucopyranosyl)-D-glucose, 3,6-anhydro-4-*O*-D-glucose, and D-glucose. *Journal of Wood and Chemical Technology*, *2*(2), 187–205.

McGee, P. A., Fowler, W. F., Unruh, C. C., & Kenyon, W. O. (1948). Investigation of the properties of cellulose oxidised by nitrogen dioxide, VI: The effect of alkali on the celluronic acids. *Journal of American Chemical Society*, *70*, 2700–2705.

McKinley, I. G., & Grogan, H. A. (1991). Consideration of microbiology in modelling the near field of a L/ILW repository. *Experientia*, *47*(6), 573–577.

Meller, A. (1960a). The chemistry of alkaline degradation of cellulose and oxidised celluloses I. *Holzforchung*, *14*, 78–89.

Meller, A. (1960b). The chemistry of alkaline degradation of cellulose and oxidised celluloses II. *Holzforchung*, *14*, 129–139.

Moreton, A. D. (1993). Thermodynamic modelling of the effect of hydroxycarboxylic acids on the solubility of plutonium at high pH. In C. G. Interrante, & R. E. Pabalan (Eds.), *Scientific bases for nuclear waste management XVI* (*Vol. 294*) (pp. 753–758). *Materials Research Society Symposium Proceedings*, Pittsburgh: Materials Research Society.

Nef, J. U. (1907). Dissociationsvorgänge in der Zuckergruppe, Erste Abhandlung: Ueber das Verhalten der Zuckerarten gegen die Fehling'sche Lösung sowie gegen andere Oxydationsmittel. *Justus Liebigs Annalen der Chemie*, *357*, 214–312.

Nef, J. U. (1910). Dissociationsvorgänge in der Zuckergruppe, Zweite Abhandlung: Über das Verhalten der Zuckerarten gegen Ätzalkalien. *Justus Liebigs Annalen der Chemie*, *376*, 1–119.

Nef, J. U., Hedenburg, O. F., & Glattfeld, J. W. E. (1917). The method of oxidation and the oxidation products of L-arabinose and of L-xylose in

alkaline solutions with air and with cupric hydroxide. *Journal of American Chemical Society*, *39*, 1638–1652.

Nevell, T. P. (1963). Oxidation. In R. L. Whistler (Ed.), *Methods in carbohydrate chemistry* (*Vol. III*) (pp. 164–185). *Cellulose*, New York: Academic Press.

Nevell, T. P. (1985a). Degradation of cellulose by acids, alkalis, and mechanical means. In T. P. Nevell, & S. H. Zeronian (Eds.), *Cellulose chemistry and its applications* (pp. 223–242). Chichester: Ellis Horwood.

Nevell, T. P. (1985b). Oxidation of cellulose. In T. P. Nevell, & S. H. Zeronian (Eds.), *Cellulose chemistry and its applications* (pp. 243–265). Chichester: Ellis Horwood.

Niemelä, K. (1987). Identification of novel cellulose degradation products. *Acta Chemica Scandinavica*, *B41*, 257–260.

Niemelä, K., Alén, R., & Sjöström, E. (1985). The formation of carboxylic-acids during Kraft and Kraft-anthraquinone pulping of birch wood. *Holzforschung*, *39*(3), 167–172.

Niemelä, K., & Sjöström, E. (1986). The conversion of cellulose into carboxylic acids by a drastic alkali treatment. *Biomass*, *11*, 215–221.

Nirex (2001a). The Nirex phased disposal concept. *Nirex Report*, N/025.

Nirex (2001b). Post-closure performance assessment. *Nirex Report*, N/031.

O'Meara, D., & Richards, G. N. (1958a). Alkaline degradation of polysaccharides, part IV: Monosaccharide analogues of periodate oxycellulose. *Journal of Chemical Society*, 1204–1211.

O'Meara, D., & Richards, G. N. (1958b). Alkaline degradation of polysaccharides, part V: Periodate oxycellulose. *Journal of Chemical Society*, 4504–4508.

Pavasars, I. (1999). *Characterisation of organic substances in waste materials under alkaline conditions*. PhD Thesis, Linköping University, Sweden.

Peligot, E. (1839). Ueber den Rohrzucker und eine neue Säure aus der Einwirkung der Alkalien auf den Stärke-zucker. *Justus Liebigs Annalen der Chemie*, *23*, 169.

Peligot, E. (1880a). Ueber einige Einschaften der Glucose. *Berichte der Deutschen Chemischen Gesellschaft*, *13*, 196–197.

Peligot, E. (1880b). Ueber das Saccharin. *Berichte der Deutschen Chemischen Gesellschaft*, *13*, 1364.

Pettersen, R. C. (1984). The chemical composition of wood. In R. Rowell (Ed.), *The chemistry of solid wood* (pp. 57–69). Washington: American Chemical Society.

Phillip, B. (1984). Degradation of cellulose—mechanisms and applications. *Pure and Applied Chemistry*, *56*(3), 391–402.

Procter, A. R., & Wiekenkamp, R. H. (1969). The stabilisation of cellulose to alkaline degradation by novel end unit modifications. *Journal of Polymer Science, Part C*, *28*, 1–13.

Rai, D., Rao, L., & Moore, D. A. (1998). The influence of isosaccharinic acid on the solubility of Np(IV) hydrous oxide. *Radiochimica Acta*, *83*, 9–13.

Redfern, P. D. (1996). *Alkaline degradation of carbohydrates*. PhD thesis, University of Birmingham, UK.

Richards, G. N. (1963). Alkaline degradation. In R. L. Whistler (Ed.), *Methods in carbohydrate chemistry* (*Vol. III*) (pp. 154–164). *Cellulose*, New York: Academic Press.

Richards, G. N. (1971). Alkaline degradation. In N. M. Bikales, & L. Segal (Eds.), *High polymers* (*Vol. V*) (pp. 1007–1014). *Cellulose and cellulose derivatives*, New York: Wiley.

Richards, G. N., & Sephton, H. H. (1957). The alkaline degradation of polysaccharides, part I: Soluble products of the action of sodium hydroxide on cellulose. *Journal of Chemical Society*, *4*, 4492–4499.

Schniewind, A. P. (1989). *Concise encyclopedia of wood and wood based materials*. London: Pergamon Press.

Shimizu, J., Kennedy, J. F., Lloyd, L. L., & Hasamudin, W. (1996). The alkaline degradation of cellulose relating to the longterm storage of radionuclides in cement. In J. F. Kennedy, G. O. Phillips, & P. A. Williams (Eds.), *The chemistry and processing of wood and plant fibrous materials* (pp. 361–368). Cambridge: Woodhead Publishing.

Sowden, J. C. (1957). The saccharinic acids. *Advances in Carbohydrate Chemistry*, *12*, 35–79.

Speck, J. C. (1958). The Lobry de Bruyn–Alberda van Ekenstein transformation. *Advances in Carbohydrate Chemistry*, *13*, 63–103.

Theander, O., & Nelson, D. A. (1988). Aqueous, high-temperature transformation of carbohydrates relative to utilisation of biomass. *Advances in Carbohydrate Chemistry and Biochemistry*, *46*, 273–326.

Treiber, E. E. (1985). Formation of fibres from cellulose solutions. In T. P. Nevell, & S. H. Zeronian (Eds.), *Cellulose chemistry and its applications* (pp. 455–479). Chichester: Ellis Horwood.

UK Patent No. 2295263, Vault backfill, UK Nirex Ltd, 9 July 1997.

Van Loon, L. C., & Glaus, M. A. (1997). Review of the kinetics of alkaline degradation of cellulose in view of its relevance for safety assessment of radioactive waste repositories. *Journal of Environmental Polymer Degradation*, *5*(2), 97–109.

Whistler, R. L., & BeMiller, J. N. (1958). Alkaline degradation of polysaccharides. *Advances in Carbohydrate Chemistry*, *13*, 289–329.

Whistler, R. L., Chang, P. K., & Richards, G. N. (1959a). Alkaline degradation of periodate-oxidised starch. *Journal of American Chemical Society*, *81*, 3133–3136.

Whistler, R. L., Chang, P. K., & Richards, G. N. (1959b). Alkaline degradation of periodate-oxidised xylan and dextran. *Journal of American Chemical Society*, *81*, 4058–4060.

de Wit, G., Kieboom, A. P. G., & van Bekkum, H. (1979). Enolisation and isomerisation of monosaccharides in aqueous, alkaline solution. *Carbohydrate Research*, *74*, 157–175.

Yang, B. Y., & Montgomery, R. (1996). Alkaline degradation of glucose: Effect of initial concentration of reactants. *Carbohydrate Research*, *280*, 27–45.

Ziderman, I. (1980). Endwise depolymerisation of cellulose in the presence of alkaline earth hydroxides. *Cellulose and Chemical Technology*, *14*, 703–711.

Ziderman, I., & Bel-Ayche, J. (1978a). Specific hydroxide ion catalysis of the endwise depolymerisation of cellulose. *Journal of Applied Polymer Science*, *22*, 711–718.

Ziderman, I., & Bel-Ayche, J. (1978b). Kinetics for unidirectional endwise chain depolymerisations: Experiments with amylose in aqueous alkaline solutions. *Journal of Applied Polymer Science*, *22*, 1151–1158.

Ziderman, I., & Bel-Ayche, J. (1986). Using disaccharides as a kinetic model for alkaline degradation of celluloses and starches. *Journal of Applied Polymer Science*, *32*, 3255–3261.