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Degradation of cellulose under alkaline conditions

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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.

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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

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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 $(1 \rightarrow 4)$-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