(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 (~280 °C), methanoic (formic), ethanoic (acetic), hydroxyethanoic (glycollic) and 2-hydroxypropanoic (lactic) acids are the major observed degradation products, ~40% based on cellulose starting weight (Krochta, Hudson, & Drake, 1984).