Review of the Kinetics of Alkaline Degradation of Cellulose in View of Its Relevance for Safety Assessment of Radioactive Waste Repositories

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The degradation of cellulose (a substantial component of low- and intermediate-level radioactive waste) under alkaline conditions occurs via two main processes: a peeling-off reaction and a base-catalyzed cleavage of glycosidic bonds (hydrolysis). Both processes show pseudo-first-order kinetics. At ambient temperature, the peeling-off process is the dominant degradation mechanism, resulting in the formation of mainly isosaccharinic acid. The degradation depends strongly on the degree of polymerization (DP) and on the number of reducing end groups present in cellulose. Beyond pH 12.5, the OH^- concentration has only a minor effect on the degradation rate. It was estimated that under repository conditions (alkaline environment, pH 13.3–12.5) about 10% of the cellulosic materials (average DP = 1000–2000) will degrade in the first stage (up to 10^5 years) by the peeling-off reaction and will cause an ingrowth of isosaccharinic acid in the interstitial cement pore water. In the second stage (10^5–10^6 years), alkaline hydrolysis will control the further degradation of the cellulose. The potential role of microorganisms in the degradation of cellulose under alkaline conditions could not be evaluated. Proper assessment of the effect of cellulose degradation on the mobilization of radionuclides basically requires knowing the concentration of isosaccharinic acid in the pore water. This concentration, however, depends on several factors such as the stability of ISA under alkaline conditions, sorption of ISA on cement, formation of sparingly soluble ISA-salts, etc. A discussion of all the relevant processes involved, however, is far beyond the scope of the presented overview.

KEY WORDS: Cellulose; alkaline degradation; peeling off; isosaccharinic acid; kinetics.

INTRODUCTION

Low- and intermediate-level radioactive waste (L/ILW) contains substantial amounts of cellulosic materials. In Switzerland, about 50% of the organic waste planned to be emplaced in the repository for low and intermediate radioactive waste (L/ILW-repository) is cellulosic [1]. The use of large amounts of cement for constructing the repository causes an alkaline environment (pH of the cement pore water remains above 12.5 for periods of the order of 10^5 years [2]). It is well-known in the literature that cellulose is unstable under alkaline conditions and will degrade to water-soluble, low molecular weight compounds [3]. The type of degradation products formed depends strongly on the composition of the solution in contact with the cellulose. In the presence of Ca^{2+}, a primary cation in cement pore water, isosaccharinic acid (ISA) will be the main degradation product [4, 5]. Isosaccharinic acid (Fig. 1) is assumed to form—in analogy with gluconic acid (Fig. 1)—stable complexes with tri- and tetravalent radionuclides such as Am^{3+} and Pu^{4+} [6–8] and might lower their sorption on the cement phase [9]. This would lead to an enhanced release of such radionuclides to the geo- and biosphere.

When trying to assess the potential effect of the

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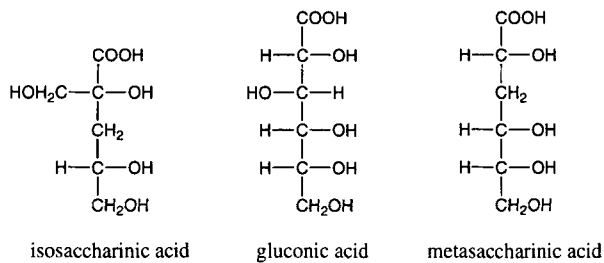[2] To whom correspondence should be addressed.

Fig. 1. Chemical structures of isosaccharinic acid, gluconic acid, and metasaccharinic acid.

presence of cellulose in a repository, it is very important to have an idea of the concentration range of ISA in the cement pore water, because the concentration of a ligand, together with the stability of the complex formed, is one of the key parameters governing the ultimate effect of complexation on sorption. The concentration of ISA in the cement pore water depends on several factors, such as the

- amount of cellulose emplaced in the cement (cellulose loading),
- degradation kinetics of cellulose,
- stability of ISA formed,
- sorption of ISA on the cement phase, and
- formation of sparingly soluble ISA-salts with, e.g., calcium.

The first two factors are directly related to the degradation of cellulose, whereas the others have to do with the properties of the degradation product itself or with the interaction between the degradation product and repository components and, consequently, are not directly related to the degradation of cellulose. In this overview, we focus only on the factors that are directly related to the degradation process of cellulose.

Bradbury and Sarott [9] assumed, in their overview of sorption of radionuclides on cement, that the degradation of cellulose occurs instantaneously and completely and that isosaccharinic acid is the main degra-

dation product. The ISA concentration based on this assumption depends on the cellulose content of the repository. High cellulose contents lead to ISA concentrations high enough (up to 0.1 M) to complex virtually all of the radionuclides present so that no sorption occurs. Such an assumption is very conservative. A more realistic picture, however, can be obtained when information on the following questions is available and taken into account:

- Is the degradation of cellulose such a fast process that it is reasonable to assume an instantaneous degradation? and
- Will cellulose be degraded completely to ISA?

In the following, we try to answer these questions based on information available in the literature. We discuss the mechanisms and kinetics of the alkaline degradation of cellulose in detail w.r.t. their consequences on the long-term degradation of cellulose in a cementitious repository.

CELLULOSE

Cellulose is the most abundant organic material on earth. It is the main component of plant sources, serving as the structural material by which plants, trees, and grasses sustain the strength to stay upright. It occurs in almost-pure form in cotton fibers (90%) and, to a lesser extent, in flax (80%), jute (60–70%), and wood (40–50%). Cellulose is a linear macromolecule composed of up to 10,000 (1,4)-β-D-glucopyranose units (Fig. 2), and only the configuration of the C_1 position is different from that of amylose that is made of (1,4)-α-D-glucopyranose [10].

The cellulose molecule has a nonreducing end and a reducing one. The reducing end is a latent aldehyde and, like an aldehydo function, responds to both reduction and oxidation processes. As will be seen later, the reducing end group plays a key role in the alkaline deg-
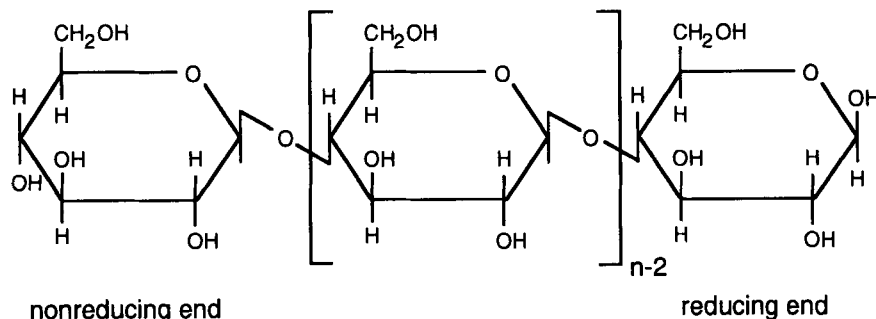

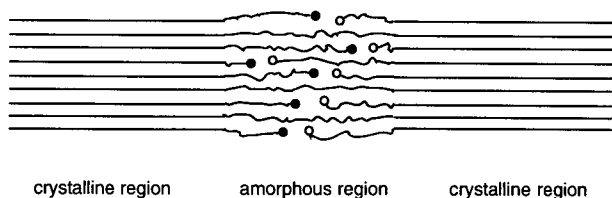Fig. 2. Chemical structure of cellulose.

Fig. 3. Microfibrillic structure of cellulose [12]. (●) Reducing end group; (○) nonreducing end group.

radation of cellulose. The cellulose molecular chains are ordered into strands as cellulose microfibrils through inter- and intramolecular hydrogen bonding [11]. These microfibrils have crystalline and amorphous regions (Fig. 3). The alkaline degradation takes place in the amorphous regions of cellulose [12, 13].

CEMENT PORE WATER

The chemistry of cement pore water has been discussed in detail by Berner [2] and Neall [14]. The composition is determined to a large extent by the composition of the cement and the water flow through the repository. The evolution of the pore water chemistry can be grossly divided into three stages. In the first stage, the dissolution of NaOH and KOH—present in cement as "impurities"—causes a (Na,K)OH cement pore water saturated with respect to $Ca(OH)_2$. The pH of this initial pore water lies around 13.4 (the concentration of OH^- is 0.3 M) and the Ca concentration is about 2 mM. In the second stage, when all NaOH and KOH has been leached out, the composition of the pore water is determined by the dissolution of $Ca(OH)_2$. The pH of the pore water falls to 12.5 and the Ca concentration lies around 20 mM. In the third stage—when all the $Ca(OH)_2$ has dissolved—the pH falls further and hydrated Ca–Si phases (CSH-gels) start dissolving.

Based on assumptions made for the water flow and the permeability and porosity of the cement, the pH of the cement pore water was calculated to remain above 12.5 for periods of the order of 10^5 years [2].

DEGRADATION OF CELLULOSE UNDER ALKALINE CONDITIONS

Peeling-Off Reaction

General

The peeling-off reaction is an endwise degradation process by which a reducing end group is split off from the cellulose chain, resulting in soluble degradation products such as isosaccharinic acid. The peeling-off reaction is controlled by two competing reactions: a progressive shortening of the cellulose molecule in which glucose units are progressively eliminated from the cellulose molecule (starting at the reducing end group) and a stopping reaction in which the reducing end group is converted to an alkalistable end group while it is still attached to the cellulose chain. The stopping reaction can be subdivided into a *chemical* and a *physical stopping* reaction. The former is the transformation of a reducing end group into a stable metasaccharinic acid (Fig. 1) end group. The latter implies that a reducing end group reaches the crystalline region of the cellulose and is no longer accessible to alkali [12]. The physical stopping reaction is not an abrupt process since there is a gradual transition from the amorphous to the crystalline region rather than a distinct interface. A schematic presentation of the peeling-off reaction is given in Fig. 4.

General Reaction Kinetics

The kinetics of the peeling-off reaction of cellulose have been studied in detail by Haas *et al.* [12]. They performed kinetic studies on hydrocellulose (prepared from cotton) with a degree of polymerization (DP) of 166 at different temperatures (ranging from 65 to 132°C) in 1.25 M NaOH solutions. The liquid/solid ratio in their studies was so high (100/1) that the NaOH concentration remained practically constant during the whole reaction time.

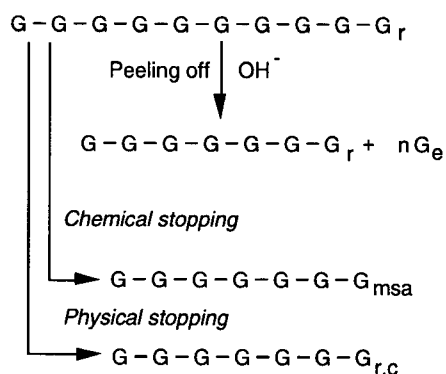For the progressive chain degradation, at a constant concentration of OH^-, the following equation can be

Fig. 4. Schematic presentation of the peeling-off reaction. G is a glucose monomeric unit (glucopyranose), G_{msa} is a stable metasaccharinic acid end group, G_e is a glucose unit eliminated, and n is the number of glucose units eliminated. G_r is a reducing end group in the amorphous region of the cellulose fiber and $G_{r,c}$ is a reducing end group in the crystalline region of the cellulose fiber.

written:

$$\frac{d(G_e)}{dt} = k_1 \cdot (G_r) \quad (1)$$

with (G_e) the mole fraction of glucose units eliminated, (G_r) the mole fraction of reducing end groups available for the reaction, and k_1 the pseudo-first-order rate constant. The mole fraction of a component is defined here as the number of moles of that component divided by the number of moles of all components in the system. For the system with cellulose described here, the number of moles of all components equals the initial degree of polymerization (DP_0). As an example, the mole fraction of G_e is defined as

$$(G_e) = \frac{G_e}{DP_0} \quad (2)$$

Assuming that the glucose units are eliminated as isosaccharinic acid (no fragmentation reaction),[3] Eq. (1) can also be written as

$$\frac{d(ISA)}{dt} = k_1 \cdot (G_r) \quad (3)$$

where (ISA) is the mole fraction of isosaccharinic acid formed.

For the chemical stopping reaction, the following rate equation can be written:

$$\frac{d(MSA)}{dt} = k_2 \cdot (G_r) \quad (4)$$

where (MSA) is the mole fraction of stable metasaccharinic acid end groups formed and k_2 the pseudo-first-order rate constant for the chemical stopping reaction.

Although no chemical reaction is involved in the physical stopping process, a similar rate equation can be written for this physical stopping reaction:

$$\frac{d(G_t)}{dt} = k_{cr} \cdot (G_r) \quad (5)$$

where (G_t) is the mole fraction of reducing end groups not available for reaction and k_{cr} is the formal rate constant of termination caused by inaccessibility.

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[3] In the peeling-off reaction, the reducing end group is split off from the cellulose chain, resulting in the formation of an intermediate product G_e. The intermediate product reacts further via two reaction pathways to give the ultimate degradation products. Isosaccharinic acid is formed via an internal rearrangement of the intermediate product (benzilic acid type of rearrangement). Via a fragmentation reaction the intermediate molecule is split into smaller molecules such as lactic acid, formic acid, and acetic acid [3–5, 15, 16].

The decrease in reactive reducing end groups is caused by the two stopping reactions and can be combined as

$$-\frac{d(G_r)}{dt} = k_2 \cdot (G_r) + k_{cr} \cdot (G_r) = k_t \cdot (G_r) \quad (6)$$

where k_t ($k_t = k_2 + k_{cr}$) is the total rate constant for chain termination.

At $t = 0$, $(G_r) = (G_r)_0$, the initial reducing end-group content. Integration of Eq. (6) gives

$$(G_r) = (G_r)_0 \cdot e^{-k_t \cdot t} \quad (7)$$

Substitution of Eq. (7) in Eqs. (1) and (3) gives

$$\frac{d(G_e)}{dt} = k_1 \cdot (G_r)_0 \cdot e^{-k_t \cdot t} \quad (8)$$

$$\frac{d(ISA)}{dt} = k_1 \cdot (G_r)_0 \cdot e^{-k_t \cdot t} \quad (9)$$

At $t = 0$, (G_e) and (ISA) $= 0$ and Eqs. (8) and (9), after integration, give

$$(G_e) = \frac{k_1}{k_t} (G_r)_0 \cdot (1 - e^{-k_t \cdot t}) \quad (10)$$

$$(ISA) = \frac{k_1}{k_t} (G_r)_0 \cdot (1 - e^{-k_t \cdot t}) \quad (11)$$

Substitution of Eq (7) in Eqs. (4) and (5) gives

$$\frac{d(MSA)}{dt} = k_1 \cdot (G_r)_0 \cdot e^{-k_t \cdot t} \quad (12)$$

and

$$\frac{d(G_t)}{dt} = k_{cr} \cdot (G_r)_0 \cdot e^{-k_t \cdot t} \quad (13)$$

At $t = 0$, (MSA) and $(G_t) = 0$ and integration of Eqs. (12) and (13) gives

$$(MSA) = \frac{k_2}{k_t} (G_r)_0 \cdot (1 - e^{-k_t \cdot t}) \quad (14)$$

and

$$(G_t) = \frac{k_{cr}}{k_t} (G_r)_0 \cdot (1 - e^{-k_t \cdot t}) \quad (15)$$

The maximum amount of (ISA) at $t = \infty$ can be calculated from Eq. (11):

$$(ISA)_{max} = \frac{k_1}{k_t} (G_r)_0 \quad (16)$$

The maximum amount of cellulose degraded equals the maximum amount of glucose units peeled off and can

be written as

$$(\text{cellulose degraded})_{max} = (G_e)_{max} = \frac{k_1}{k_t} (G_r)_0 \quad (17)$$

From Eqs. (16) and (17) it can be deduced that $(ISA)_{max}$ and $(\text{cellulose degraded})_{max}$ depend on the initial mole fraction of reducing end groups in the cellulose, $(G_r)_0$, and on the ratio of the rate constants of the propagation reaction and the stopping reactions.

The initial mole fraction of reducing end groups is defined as

$$(G_r)_0 = \frac{\text{moles of reducing end groups}}{\text{moles of glucose units in the chain}} \quad (18)$$

The mole fraction of reducing end groups depends on the average amount of reducing end groups in a cellulose molecule and on the degree of polymerization. Both these parameters have an effect on the amount of cellulose that will be degraded. In theory, one molecule of cellulose, containing n glucose units (degree of polymerization DP = n), has one reducing end group. In reality, not all cellulose molecules will have reducing end groups because the reducing end groups may have been transformed to nonreducing end groups during the pulping process [17–20]. Consequently, the mole fraction of reducing end groups in cellulose with DP = n is

$$0 \le (G_r)_0 \le \frac{1}{n} \quad (19)$$

The presence of one reducing end group per cellulose molecule will result in the maximum value of the concentration of reducing end groups $(G_r)_0$ for a cellulose molecule with DP = n and, consequently, results in the upper limit of the maximum amount of degradable cellulose.

The amount of isosaccharinic acid formed and also the amount of cellulose degraded by the peeling off reaction depend strongly on the degree of polymerization of cellulose. The larger the cellulose molecule, the lower the mole fraction of reducing end groups [as can be seen from Eq. (18)] and the lower the extent of degradation (Fig. 5).

Effect of Temperature on the Peeling-Off Reaction Kinetics

The rate constants k_1, k_2, k_{cr}, and k_t were determined by Haas *et al.* [12] at different temperatures between 65 and 132°C and an OH$^-$ concentration of 1.25 M. The authors used hydrocellulose with DP = 166. The values are summarized in Table I.
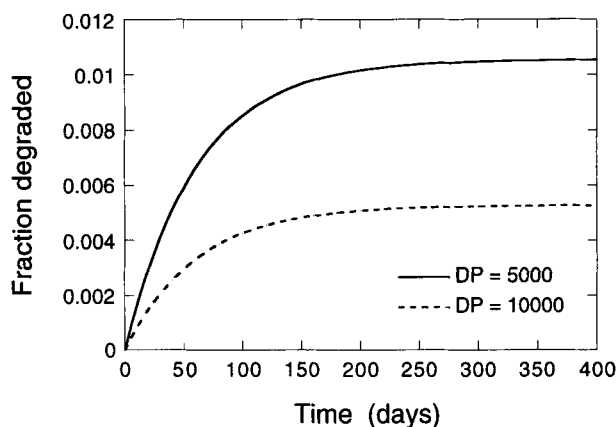

Fig. 5. Degradation of cellulose as a function of time at [OH$^-$] = 0.3 M and 25°C for different degrees of polymerization (DP). The solid lines were calculated using Eq. (10), with $k_1 = 3.65 \cdot 10^{-2}$ h^{-1} and $k_t = 6.91 \cdot 10^{-4}$ h^{-1}.

Values of these constants at lower temperatures can be estimated by applying the Arrhenius equation:

$$k = A \cdot e^{-E_a/R \cdot T} \quad (20)$$

or, in the linear form,

$$\log k = \log A - 0.434 \cdot \frac{E_a}{R \cdot T} \quad (21)$$

with

A = Arrhenius parameter (h^{-1})
k = rate constant (h^{-1})

Table I. Overview of the Rate Constants for Cellulose Degradation (Peeling-Off Reaction) at Different Temperatures in 1.25 M NaOH [12]

T (°C)	k_1 (h^{-1})	k_2 (h^{-1})	k_{cr} (h^{-1})	k_t (h^{-1})
25[a]	0.0393	0.000014	0.00073[b]	0.00074
65	4	0.0041	0.057	0.061
78	17.8	0.031	0.263	0.29
87	46.3	0.097	0.64	0.74
100	147	0.50	1.60	2.10
132	1550	6.98	13.0	19.98

[a] Extrapolated by the Arrhenius equation (21):

$\log k_1 = 16.21 - 5249 \cdot 1/T \rightarrow \log k_1$ (25°C) = -1.41 ± 0.35
$\log k_2 = 17.12 - 6548 \cdot 1/T \rightarrow \log k_2$ (25°C) = -4.86 ± 0.46
$\log k_t = 13.86 - 5062 \cdot 1/T \rightarrow \log k_t$ (25°C) = -3.13 ± 0.44

[b] The value of k_{cr} at 25°C was calculated from the extrapolated values k_t and k_2 by using the equation $k_{cr} = k_t - k_2$ because k_{cr} is not a measured value but calculated from k_t and k_2.

E_a = activation energy (J · mol^{-1})

R = universal gas constant (J · mol^{-1} · K^{-1})

T = absolute temperature (K)

Plotting log k versus the reciprocal absolute temperatures yields a straight line with slope 0.434 · E_a/R and intercept log A with the Y-axis. With these equations, values for k_1, k_2, and k_t at 25°C were calculated (see Table I). The errors on the estimated values were calculated from the errors on the slope and the intercept of the regression line [21], the Student t value for (n − 1) = 4 degrees of freedom, and the 95% confidence level. Figure 6 illustrates the Arrhenius equation for the different reactions of the peeling off process. It is clearly shown that the relationship between the logarithm of the rate constants and the reciprocal of the absolute temperature is a linear one according to Eq. (21). The activation energy (E_a) of the different reactions can be calculated from the slope of the lines. The propagation reaction has an activation energy of 101 kJ · mol^{-1} and the activation energy of the overall stopping reaction is 97 kJ · mol^{-1}.

The extent of cellulose degradation by the peeling-off reaction depends on the ratio of the rate constants k_1/k_t [Eq. 17] and, consequently, on the reaction temperature. At lower temperatures, the degree of degradation is smaller than at higher temperatures. This can be explained properly by the slightly higher activation energy of the propagation reaction w.r.t. the overall stopping reaction.
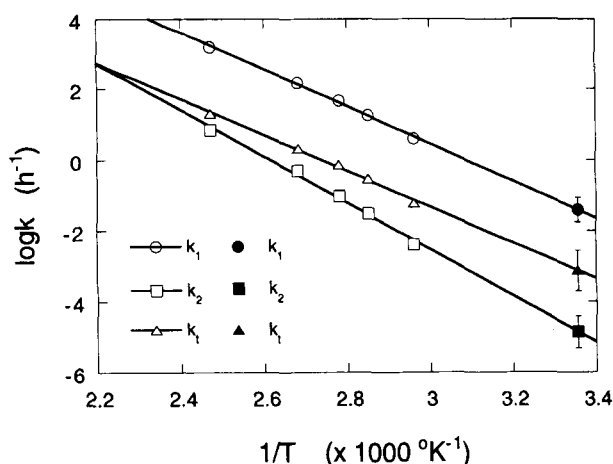

Fig. 6. Arrhenius plot for the peeling-off reaction [chain propagation (k_1), chemical (k_2) and overall (k_t) stopping reaction] of cellulose in 1.25 M NaOH. Open symbols represent experimental data [12]; filled symbols are extrapolated values. The error bars on the extrapolated values represent the 95% confidence level estimated from the error on the slope and the intercept of the regression line.

Effect of Base Concentration on the Peeling-Off Reaction Kinetics

The concentration of OH$^-$ in the cement pore water in the initial stage of cement degradation is about 0.3 M and the Ca level is about 2 mM. To evaluate the degradation of cellulose under such repository conditions, the effect of pH (or OH$^-$ concentration) and the effect of Ca^{2+} on the peeling-off reaction have to be discussed. The rate constants discussed in the previous section were derived for reaction conditions of 1.25 M NaOH in the absence of Ca. No further systematic studies on the effect of [OH$^-$] and [Ca^{2+}] on the rate constants (k_1, k_2, k_{cr}, and k_t) have been found in the literature for cellulose. Although no experimental data on the effect of OH$^-$ and Ca^{2+} are available for cellulose, some data exist for other polymeric materials. Studies on amylose [22] and β-(1-3)-glucans [23] showed that the hydroxyl ion does not participate in the rate-determining reaction step and that anionic species are involved in the peeling-off and chemical stopping reaction for these polysaccharides. It was further shown that the alkaline degradation of amylose with α-(1-4)-glycosidic bonds (at temperatures < 120°C) proceeds by the same reaction mechanisms as the alkaline degradation of cellulose with β-(1-4)-glycosidic bonds [22], i.e.,

* a chain propagation reaction (peeling off reaction), resulting in the formation of isosaccharinic acid; and
* a chemical stopping reaction by which the reducing end group is transformed into an alkali-stable metasaccharinic acid end group.

A physical stopping reaction does not occur because amylose does not have a microfibrillar structure such as cellulose. Conclusions drawn from the study on amylose [22] are applicable to a large extent to cellulose.

The rate constant for the peeling-off reaction (k_1) increased with the concentration of OH$^-$ until 0.3 M. Beyond 0.3 M, k_1 remained constant (see Fig. 7). The rate constant for the chemical stopping reaction (k_2) was negligibly small for a concentration of OH$^-$ below 0.1 M and could not be quantified. Beyond 0.3 M, k_2 increased until the concentration of OH$^-$ reached a value of 1.5 M. Beyond 1.5 M, k_2 remained constant. It was also observed that up to 0.1 M, amylose was completely degraded and that, for 0.1 M < [OH$^-$] < 1.5 M, the extent of degradation decreased. Beyond 1.5 M, the extent of degradation remained constant [22].

In analogy to amylose, it is assumed that the reactivity of the reducing end group in cellulose is proportional to its degree of ionization:
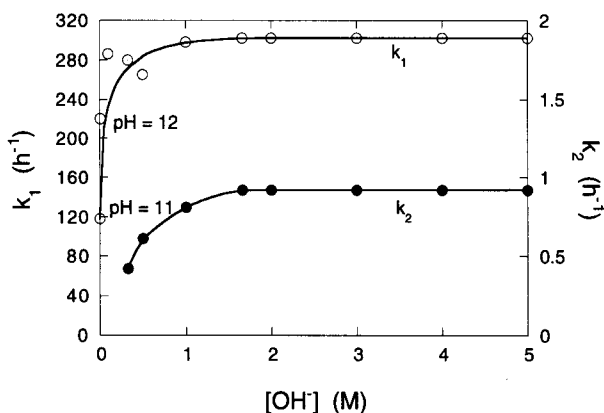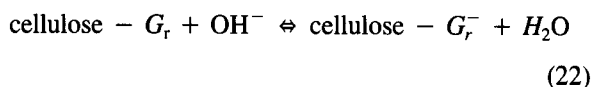
Fig. 7. Dependence of rate constants for the peeling-off reaction (k_1) and chemical stopping reaction (k_2) of amylose on the hydroxyl concentration at 100°C [22].

$$\text{cellulose} - G_r + OH^- \leftrightarrow \text{cellulose} - G_r^- + H_2O \tag{22}$$

The deprotonation constant is defined as

$$K_1 = \frac{(G_r^-)}{(G_r) \cdot [OH^-]} \tag{23}$$

where (G_r^-) is the mole fraction of deprotonated reducing end groups and (G_r) is the mole fraction of protonated reducing end groups.

From the mass balance,

$$(G_r)_t = (G_r) + (G_r^-) \tag{24}$$

and Eq. (23), it can be shown that

$$(G_r^-) = \frac{K_1 \cdot [OH^-]}{1 + K_1 \cdot [OH^-]} \cdot (G_r)_t \tag{25}$$

The rate equation for the propagation reaction can be written as

$$\frac{d(G_e)}{dt} = k_1' \cdot (G_r^-) \tag{26}$$

where k_1' is the OH-independent first-order rate constant for the peeling-off reaction. Combining Eqs. (25) and (26) results in

$$\frac{d(G_e)}{dt} = k_1' \cdot \frac{K_1 \cdot [OH^-]}{1 + K_1 \cdot [OH^-]} \cdot (G_r)_t \tag{27}$$

With

$$k_1 = k_1' \cdot \frac{K_1 \cdot [OH^-]}{1 + K_1 \cdot [OH^-]} \tag{28}$$

Eq. (27) can be written as

$$\frac{d(G_e)}{dt} = k_1 \cdot (G_r)_t \tag{29}$$

where k_1 is the "conditional" OH-dependent rate constant.

Equation (29) is very similar to Eq. (1). The formalism developed by Haas *et al.* [12] for the peeling-off reaction was a special case of the more general formalism presented by Eq. (27) because their studies were performed at a high and constant concentration of OH^-.

For the stopping reaction, a further deprotonation of the reducing end group is required so that a second deprotonation step has to be introduced. The rate equation for the chemical stopping reaction can be written as

$$\frac{d(MSA)}{dt} = k_2' \cdot (G_r^{2-}) \tag{30}$$

where k_2' is the OH-independent first-order rate constant for the chemical stopping reaction and (G_r^{2-}) the mole fraction of twofold deprotonated reducing end groups.

Since at low temperatures the chemical stopping reaction plays a minor role in the overall stopping reaction of the alkaline degradation of cellulose (see Table I, $k_2 \ll k_{cr}$), the dependence of k_2 on the hydroxyl concentration is not discussed further here.

The effect of $[OH^-]$ on the physical stopping reaction was not studied by Lai and Sarkanen [22] because, as already mentioned, such a stopping process does not occur in amylose. For cellulose, however, the following rate equation—based on Eq. (5)—can be written assuming that the reaction rate is proportional to the mole fraction of deprotonated end groups:

$$\frac{d(G_t)}{dt} = k_{cr}' \cdot \frac{K_1 \cdot [OH^-]}{1 + K_1 \cdot [OH^-]} (G_r)_t \tag{31}$$

with

$$k_{cr} = k_{cr}' \cdot \frac{K_1 \cdot [OH^-]}{1 + K_1 \cdot [OH^-]} \tag{32}$$

Equation (31) is similar to Eq. (27) for the peeling-off reaction. This similarity can be justified as follows. Since the physical stopping reaction occurs when a reducing end group reaches the crystalline region of the cellulose fiber, its rate will depend strongly on the rate of the peeling-off reaction. The faster the peeling-off reaction, the faster a reducing end group will reach the crystalline region. Consequently, the rates of both reactions have to be strongly correlated. The ratio k_1'/k_{cr}' is constant and equals k_1/k_{cr}.

From the considerations made above, the maximum amount of cellulose that will be degraded can be

written as

$$(\text{cellulose degraded})_{max} = (G_e)_{max} = \frac{k_1'}{k_t'}(G_r)_0 \quad (33)$$

where k_1' and k_t' are the intrinsic (i.e., OH-independent) rate constants. Because of the assumption that the rate of stopping is proportional to the rate of degradation, the extent of cellulose degradation is independent of the OH^- concentration. This was experimentally confirmed by Machell and Richards [24], who did not see an effect of the alkali concentration on the extent of cellulose degradation in the range $0.125\,M < [OH^-] < 1.25\,M$. For a concentration of OH^- higher than $2\,M$, a significant effect of $[OH^-]$ on the extent of degradation was observed. At these concentrations, however, the structure of cellulose is changed (transition of crystalline to amorphous cellulose), resulting in a higher accessability of the cellulose to OH^- [25].

The reaction rate, however, depends on the concentration of OH^-. The values of the first-order rate constants for cement pore water conditions (i.e., $[OH^-]$ = $0.3\,M$) can be calculated by applying the following equation:

$$k_{i,0.3} = k_i' \cdot \frac{K_1 \cdot [OH^-]}{1 + K_1 \cdot [OH^-]} \quad (34)$$

with

$k_{i,0.3}$ = rate constant for $[OH^-]$ = $0.3\,M$

k_i' = intrinsic rate constant

$[OH^-]$ = concentration of OH (M)

K_1 = deprotonation constant for the deprotonation of C_1-OH of the reducing end group ($K_1 \approx 30$)

The values of k_i' were calculated by applying Eq. (34) for $[OH^-]$ = $1.25\,M$ and the values of $k_{i,1.25}$ at $25\,°C$ as summarized in Table I.

The values of the different rate constants for $0.3\,M$ OH^- and $25\,°C$ are summarized in Table II. The differ-

ence in rate constant between 1.25 and $0.3\,M$ OH^- is very small because K_1 of the reducing end group is ≈ 30 or the deprotonation constant pK_a = 12.5 [22, 23, 26]. Beyond pH 13, the reducing end groups are almost completely deprotonated.

Effect of Ca^{2+} on the Peeling-Off Reaction Kinetics

Ca^{2+} has a significant effect on the peeling-off reaction [4, 5, 24, 27]. Ca^{2+} seems to catalyze the benzilic acid type of rearrangement, leading to the formation of ISA. Also, the chemical stopping reaction is catalyzed. The overall effect of the presence of Ca^{2+} is a lower degree of degradation and the formation of relatively more ISA at the expense of side products. No systematic kinetics studies on the alkaline degradation of cellulose in presence of Ca^{2+} have been performed.

Base-Catalyzed Cleavage of Glycosidic Bonds (Alkaline Hydrolysis)

General Mechanisms and Reaction Kinetics

Besides the peeling-off reaction, the base-catalyzed cleavage of glycosidic bonds is another important process in the alkaline degradation of cellulose that needs to be discussed in detail. The kinetics of alkaline hydrolysis have been studied by Lai and Sarkanen [28], Lai [29], and Franzon and Samuelson [30].

Alkaline hydrolysis of cellulose could not be studied separately from the peeling-off reaction because hydrolysis produces new reducing end groups, initiating a peeling off reaction.

As illustrated in Fig. 8, the degradation is initiated by cleavage of a glycosidic bond. The newly formed reducing end groups give rise to a chain degradation
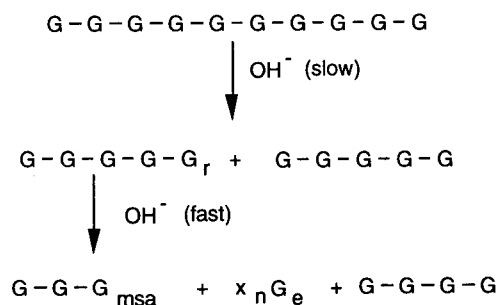
Table II. Overview of the Rate Constants for Cellulose Degradation by the Peeling-Off Reaction for 25°C and Different OH^- Concentrations

$[OH^-]$ (M)	k_1 (h^{-1})	k_2 (h^{-1})	k_{cr} (h^{-1})[a]	k_t (h^{-1})
1.25	3.93E-2	1.40E-5	7.31E-4	7.45E-4
0.3[b]	3.65E-2	1.30E-5	6.78E-4	6.91E-4

[a]$k_{cr} \approx k_t - k_2$.
[b]Calculated by Eq. (34).

$$G - G - G - G - G - G - G - G - G - G$$
$$\downarrow OH^- \text{ (slow)}$$
$$G - G - G - G - G_r \quad + \quad G - G - G - G - G$$
$$\downarrow OH^- \text{ (fast)}$$
$$G - G - G_{msa} \quad + \quad x_n G_e \quad + \quad G - G - G - G$$

Fig. 8. Schematic overview of the alkaline degradation of cellulose by the base-catalyzed cleavage of glycosidic bonds and the peeling-off reaction. G_r = reducing end group, G_{msa} = alkali-stable metasaccharinic acid end group, G_e = glucose units eliminated as ISA or other products; and x_n = the number of peeled-off glucose units.

(peeling-off) process by progressively converting the terminal units to isosaccharinic acid and other products (see previous section).

A few mechanisms are known for the base-catalyzed cleavage of glycosidic linkages. For cellulose, an internal nucleophilic substitution (SN_i) was found to be the most evident one [29]. The SN_i mechanism for base-catalyzed cleavage of glycosidic bonds can be divided into two processes [31]. In the first step, a deprotonation reaction occurs:

$$GlcOH + OH^- \xleftrightarrow{K} H_2O + GlcO^- \quad (35)$$
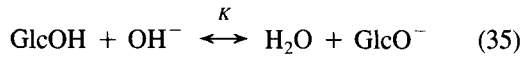
In the second step, the intermediate product $(GlcO^-)$ is transformed:

$$GlcO^- \xrightarrow{k} \text{degradation products } (P) \quad (36)$$
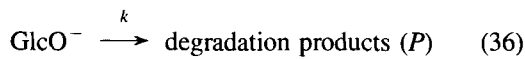
where GlcOH is the glycoside (cellulose in our case) and $GlcO^-$ is the anionic intermediate. K is the equilibrium constant between neutral and ionic glycosides (deprotonation constant) and k is the specific rate constant in the conversion of anionic intermediates to degradation products. The latter is the rate-determining step in the overall reaction. The rate of alkaline degradation of glycosides can be expressed as

$$\frac{d(P)}{dt} = k \cdot (GlcO^-) \quad (37)$$

where (P) represents the mole fraction of glycosides reacted after time t (or the mole fraction of degradation products formed) and $(GlcO^-)$ is the mole fraction of ionized, intermediate glycosides at time t.

The "deprotonation" constant K is defined as

$$K = \frac{(GlcO^-)}{\{(GlcOH)_0 - (GlcO^-) - (P)\} \quad [OH^-]} \quad (38)$$

where $(GlcOH)_0$ is the mole fraction of glycosides at $t = 0$. Combination of Eqs. (37) and (38) yields a rate equation, which is integrated to give

$$\ln \frac{(GlcOH)_0 - (P)}{(GlcOH)_0} = -\frac{K \cdot k \cdot [OH^-]}{1 + K \cdot [OH^-]} \cdot t \quad (39)$$

If

$$k_{obs} = \frac{K \cdot k \cdot [OH^-]}{1 + K \cdot [OH^-]} \quad (40)$$

where k_{obs} is the pseudo-first-order rate constant of the reaction, Eq. (39) becomes

$$\ln \frac{(GlcOH)_0 - (P)}{(GlcOH)_0} = -k_{obs} \cdot t \quad (41)$$

Franzon and Samuelson [30] studied the alkaline degradation of cellulose at 170°C in 1.25 M NaOH. They observed a change in DP of the cellulose and a weight loss. The overall degradation was found to be the result of two processes: the cleavage of glycosidic bonds (resulting in a decrease in DP), followed by a peeling-off reaction starting from the newly created reducing end group (resulting in weight loss). The amount of cellulose units peeled off after each chain break (x_n) was shown to be constant $(x_n = 65)$ and independent of the DP within a wide range. The rate-controlling step in the overall degradation process is the cleavage reaction.

The amount of cellulose left after degradation (Y) was found to be related to the degradation time (t) by the following equation:

$$\ln (Y) = -k \cdot t \quad (42)$$

with

Y = fraction of cellulose left
k = rate constant (h^{-1})
t = time (h)

Lai and Sarkanen [28] studied the alkaline degradation of cellulose at different temperatures between 146 and 186°C in 1.25 M NaOH. They came to conclusions similar to those of Franzon and Samuelson [30] and showed that the rate of degradation conformed with the following equation:

$$\ln (Y) = -k_{obs} \cdot x_n \cdot t \quad (43)$$

with

Y = fraction of unreacted cellulose
t = time (h)
k_{obs} = rate constant (h^{-1})
x_n = average number of glucose units peeled off $(x_n = 65)$

Equations (42) and (43) are very similar. Since the number of glucose units peeled off for each chain break (x_n) is constant, it can be integrated in the rate constant as was done by Franzon and Samuelson [30]:

$$k_{obs} \cdot x_n = k \quad (44)$$

Effect of Temperature on the Reaction Kinetics

Lai and Sarkanen [28] determined the rate constants for the degradation of cellulose in 1.25 M NaOH at different temperatures between 146 and 185°C. Table III summarizes their results. A rate constant for 25°C was calculated by applying the Arrhenius equation [see Eq. (21)]. Figure 9 illustrates the temperature dependence of the rate constant. At a temperature of 25°C,

Table III. Rate Constants for Degradation of Cellulose in 1.25 M OH (from Ref. 28 with the Exception of the Data for 170°C, from Ref. 30)

Temperature (°C)	$k_{obs} \cdot x_n$ (h^{-1})
25[a]	$2.17 \cdot 10^{-10}$
146	$4.00 \cdot 10^{-3}$
165	$23.0 \cdot 10^{-3}$
170	$38.7 \cdot 10^{-3}$
185	$129 \cdot 10^{-3}$

[a]Extrapolated by applying the Arrhenius equation (21): $\log(k_{obs} \cdot x_n)$ = $15.41 - 7461 \cdot 1/T \rightarrow \log(k_{obs} \cdot x_n) = -9.66 \pm 0.17$.

the rate constant is about 7 orders of magnitude lower than at 146°C. The base-catalyzed cleavage of glyco-sidic bonds is very sensitive to temperature.

Effect of Base Concentration on the Reaction Kinetics

Lai and Sarkanen [28] found a linear dependence of $k_{obs} \cdot x_n$ on the concentration of OH$^-$ for 0 M < [OH] < 2 M. Figure 10 illustrates this dependence for the degradation of cellulose at 185°C. Assuming that a similar linear relationship is valid for lower reaction temperatures, a rate constant for the degradation of cel-lulose in 0.3 M OH$^-$ at 25°C can be calculated by ap-plying the following equation:

$$k_{obs,0.3} \cdot x_n = \frac{k_{obs,1.25} \cdot x_n}{1.25} \cdot 0.3 \qquad (45)$$

and results in a value of $k_{obs} \cdot x_n = 5.25 \cdot 10^{-11}$ h^{-1} for 25°C.
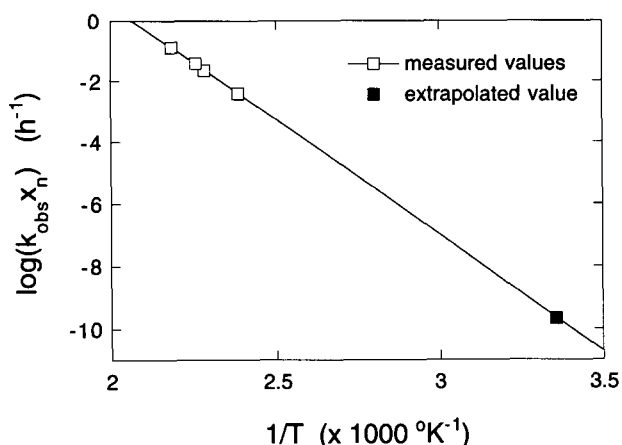

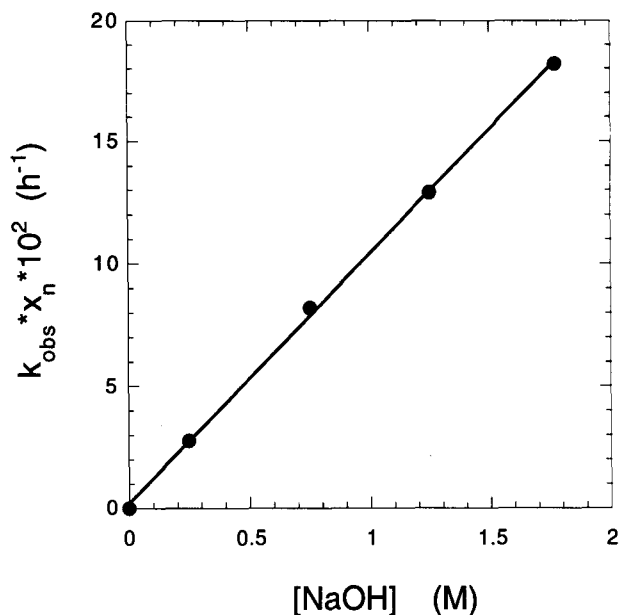**Fig. 9.** Arrhenius plot for the alkaline hydrolysis of cellulose in 1.25 M OH [28, 30].

Fig. 10. Dependence of $k_{obs} \cdot x_n$ on the concentration of OH$^-$ at 185°C [28].

Effect of Ca^{2+} on the Reaction Kinetics

No information is available on the possible effect of Ca^{2+} on the base-catalyzed hydrolysis of cellulose.

RELEVANCE FOR PERFORMANCE ASSESSMENT

In earlier safety assessment studies [1, 9], it was assumed that cellulose was degraded instantaneously and completely to isosaccharinic acid, resulting in high con-centrations of ISA in the cement pore water. From the kinetic data discussed in this work, it is clear that this is not the case. Depending on the DP of the cellulose and on the number of reducing end groups, only a small fraction of cellulose will degrade almost instantaneously to isosaccharinic acid. The rest of the cellulose will de-grade slowly by alkaline hydrolysis. In this section, we calculate the degree of degradation of cellulose (under conditions like those of a L/ILW-repository) caused by the peeling-off reaction and base-catalyzed hydrolysis, based on the information described above.

The parameters needed for calculating the degra-dation of cellulose are the kinetic parameters of the peel-ing-off reaction (k_1), the overall stopping reaction (k_t), and the alkaline hydrolysis (k_{obs}) and the mole fraction of reducing end groups ($G_r)_0$. As discussed earlier, the mole fraction of reducing end groups depends on the

Table IV. Average Degree of Polymerization (DP) of Native Cellulose of Different Origins (from Ref. 32)

Material	Average DP
Cotton fiber	14,120
Cotton fiber	5,000
Cotton fiber	10,800
Cotton fiber	5,200
Cotton fiber (seed hairs)	9,950
Cotton fiber	3,250
Ramie fiber	6,500
Ramie fiber	4,600
Bast fiber	9,550
Bast fiber	8,000
Bast fiber	9,900
Valonia	26,500
Acetobacter xylenum	5,700
Acanthamoeba castellani	2,000–6,000
Gymnosperm wood	8,450/7,800
Angiosperm wood	8,200/9,350

Fig. 11. Overall degradation of cellulose with DP = 1000 and having one initial reducing end group per cellulose molecule, at 25°C and 0.3 M OH^- as a function of time. The solid line shows the remaining cellulose calculated by Eq. (46) using $(G_r)_0 = 0.001$, $k_1 = 3.65 \cdot 10^{-2}\,h^{-1}$, $k_t = 6.91 \cdot 10^{-4}\,h^{-1}$, and $k_{obs} \cdot x_n = 5.25 \cdot 10^{-11}\,h^{-1}$.

number of reducing end groups and on the the degree of polymerization of the cellulose. The molecular weight (or degree of polymerization) of cellulose and the amount of reducing end groups depend strongly on the origin of cellulose and on the pulping process used. Consequently, it is difficult to predict the extent of cellulose degradation without making some assumptions. For the average number of reducing end groups, we take the conservative value of one per cellulose molecule. The molecular weight of native cellulose has been studied intensively. A summary overview is given by Morohoshi [32] and presented here in Table IV. Similar values were also published by Goring and Timell [33]. High-temperature pulping processes ($T > 150°C$) partially degrade native cellulose by the hydrolysis reaction, decreasing its average DP. The average DP of cellulose in paper and cotton lies around 1000–2000. A value of 1000 is taken as a representative value for cellulose present in radioactive waste. The kinetic constants summarised in Table II for $[OH^-] = 0.3\,M$ were used and it was assumed that the pH of the cement pore water stayed constant for 10^6 years.

The degradation reaction starts with the fast peeling-off reaction and stops when all reducing end groups have been transformed to stable end groups or reducing end groups no longer accessible to OH^- (after about 2 years). The further reactions are then the very slow cleavage of glycosidic bonds followed by a fast peeling-off reaction starting from the newly created reducing end groups. The overall degradation of cellulose for this case can be expressed by combining Eqs. (10) and (43) as
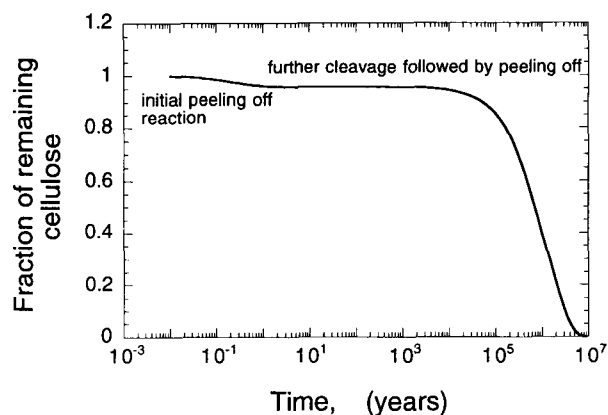
follows:

$$(\text{cellulose left}) = \frac{(1 - (k_1/k_t) \cdot (G_r)_0 \cdot (1 - e^{-k_t \cdot t}))}{e^{k_{obs} \cdot x_n \cdot t}}$$

(46)

Figure 11 illustrates the overall degradation of cellulose. In this scenario, we have a fast ingrowth of ISA in the cement pore water from the beginning on, reaching its maximum value after about 2 years. A further increase in ISA is expected to occur very slowly when the transport of ISA out of the repository is ignored.

Proper assessment of the degradation of cellulose on the fate of radionuclides in a repository requires a more detailed discussion of the concentration of ISA in the cement pore water of a repository. This concentration depends on several factors and processes such as the cellulose loading, the degradation kinetics, the solubility of sparingly soluble Ca-salts of ISA, the sorption of ISA on cement, the stability of ISA under alkaline conditions, and the water flow through the repository. Such a discussion is far beyond the scope of this paper and, therefore, will be discussed elsewhere [34, 35].

SUMMARY

Two processes are involved in the alkaline degradation of cellulose: the fast peeling-off reaction and the slow base-catalyzed cleavage of glycosidic bonds (alkaline hydrolysis).

Based on the kinetic data available for these two processes, the full degradation of cellulose under near-

field conditions existing in a cementitious L/ILW-repository ($[OH^-] = 0.3\,M$, 25°C) was estimated to take 10^5–10^6 years. In the relatively short initial stage, about 1–10% (depending on the degree of polymerization of cellulose and on the average amount of reducing end groups) of the cellulose will degrade by the peeling-off reaction and yield mainly isosaccharinic acid. After this initial stage, the degradation will continue by both base-catalyzed cleavage and the peeling-off reaction, the former controlling the overall reaction rate.

For performance assessment purposes, it can be assumed that only a part of the cellulose (1–10%) will degrade in the first 10^4 years after repository closure instead of taking a complete and instantaneous degradation. This can be justified by the kinetic data available in the literature.

The temperature has a large effect on the degradation rate of cellulose. The extent of degradation, however, is affected much less because both the propagation reaction and the stopping reaction are equally sensitive to temperature and the ratio of the two reaction rates determines the extent of degradation. Raising the temperature from 25 to 100°C will increase the extent of degradation by 30%. This is important because in the initial stage of cement hydration, the temperature is higher. The effect of temperature on cellulose degradation is limited and hence does not need to be taken into account.

Because of uncertainties in the kinetic data, additional studies on the kinetics of cellulose degradation are necessary. Especially, the effect of Ca^{2+} on the peeling-off and stopping reaction and the effect of $[OH^-]$ need to be further investigated.

ACKNOWLEDGMENTS

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