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National Cooperative for the
Disposal of Radioactive Waste

TECHNICAL REPORT 03-08

Cellulose Degradation at Alkaline Conditions:

Long-Term Experiments at Elevated Temperatures

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PREFACE

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

The work presented in this report has further been co-funded by Nirex and SKB. This report has been prepared, verified and approved for publication by PSI and Nagra. The work was carried out in accordance with quality assurance arrangements established by PSI, Nagra, Nirex and SKB. The views expressed and conclusions reached are those of the authors and do not necessarily represent those of Nagra and the co-funders.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Unit	Meaning
Celdeg	—	Fraction of cellulose reacted
Celdeg$_{DW}$	—	*Celdeg* calculated by measurement of dry weight
Celdeg$_{ISA}$	—	*Celdeg* calculated by measurement of ISA
Celdeg$_{TOC}$	—	*Celdeg* calculated by measurement of TOC
f_V	—	Correction factor for loss of water during degradation experiments
$(G_r)_0$	—	Fraction of reducing end groups
k_1	h^{-1}	Reaction rate constant for the propagation (peeling-off process)
k_t	h^{-1}	Reaction rate constant for stopping reaction (peeling-off process)
k	h^{-1}	Reaction rate constant for alkaline hydrolysis
w_C^0	g	Initial weight of cellulose added in the degradation experiments
w_C	g	Weight of undissolved cellulose in degradation experiments as a function of reaction time
$\bar{x}_n$	—	Average number of glucose units peeled-off upon chain break induced by alkaline hydrolysis
Y	—	Fraction of unreacted cellulose

Abbreviation	Meaning
ACW-I	Artificial cement pore water (representing the 'first stage' of cement degradation
CZE	Capillary zone electrophoresis
DP	Degree of polymerisation
HPAEC	High performance anion exchange chromatography
HPIEC	High performance ion exclusion chromatography
ICA	Identified carboxylic acids
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
α-ISA	α-isosaccharinic acid
β-ISA	β-isosaccharinic acid
ISA	isosaccharinic acid (where the stereochemistry is not of importance)
LdB-AvE	Lobry de Bruyn – Alberda van Ekenstein transformation
MSA	metasaccharinic acid
UICA	Unidentified carboxylic acids

ABSTRACT

The degradation of pure cellulose (Aldrich cellulose) and cotton cellulose at the conditions of an artificial cement pore water (pH 13.3) has been measured at 60 °C and 90 °C for reaction times between 1 and 2 years. The purpose of the experiments is to establish a reliable relationship between the reaction rate constant for the alkaline hydrolysis of cellulose (mid-chain scission), which is a slow reaction, and temperature. The reaction products formed in solution are analysed for the presence of the two diastereomers of isosaccharinic acid using high performance anion exchange chromatography combined with pulsed amperometric detection (HPAEC-PAD), other low-molecular weight aliphatic carboxylic acids using high performance ion exclusion chromatography (HPIEC) and for total organic carbon. The remaining cellulose solids are analysed for dry weight and degree of polymerisation. The degree of cellulose degradation as a function of reaction time is calculated based on total organic carbon and on the dry weight of the cellulose remaining.

The degradation of cellulose observed as a function of time can be divided in three reaction phases observed in the experiments: (i) an initial fast reaction phase taking a couple of days, (ii) a slow further reaction taking ~ 100 days and (iii) a complete stopping of cellulose degradation levelling-off at ~60 % of cellulose degraded. The experimental findings are unexpected in several respects: (i) The degree of cellulose degradation as a function of reaction time is almost identical for the experiments carried out at 60 °C and 90 °C, and (ii) the degree of cellulose degradation as a function of reaction time is almost identical for both pure cellulose and cotton cellulose. It can be concluded that the reaction behaviour of the materials tested cannot be explained within the classical frame of a combination of the fast endwise clipping of monomeric glucose units (peeling-off process) and the slow alkaline hydrolysis at the temperatures tested here. It may be hypothesised that the alkaline hydrolysis has even not been observed in the experiments. However, if this is true, cellulose degradation proceeded via another unknown type of reaction. Mass balances for carbon show that the large majority of reaction products found in solution can be explained by formation of isosaccharinic acids and other low-molecular weight carboxylic acids.

With respect to long-term predictions for cellulose degradation at room temperature it can be concluded that the kinetic parameters for alkaline hydrolysis as proposed in the work of PAVASARS (Linköping Studies in Arts and Science, 196, Linköping University, Sweden, 1999) are too large and that complete cellulose degradation at these temperatures occurs only within time scales larger than hundreds of years. However, it

is not possible from the experimental evidences, to corroborate the validity of a linear extrapolation ("Arrhenius equation") of the reaction rates measured at temperatures between ~140 and 190 °C to room temperature, from which it was previously concluded that complete cellulose degradation would take time spans of the order of millions of years.

An interesting observation in the present experiments is the chemical instability of α-isosaccharinic acid at 90 °C, which has been hypothetically interpreted as a fragmentation induced by the sorption of α-isosaccharinic acid on $Ca(OH)_2$. Carbon mass balances show that α-isosaccharinic acid is thereby transformed to other low-molecular weight carboxylic acids. Such a reaction would be an interesting long-term perspective for performance assessment of the disposal of cellulose-containing radioactive waste, in that it may reduce the concentration of organic compounds strongly complexing radionuclides.

ZUSAMMENFASSUNG

Der Abbau von reiner Cellulose und Baumwolle wurde unter den Bedingungen eines künstlichen Zementporenwassers (pH 13.3) bei Temperaturen von 60 °C und 90 °C über Zeiträume von 1 bis 2 Jahren verfolgt. Ziel der Experimente ist es, einen verlässlichen Zusammenhang zwischen Temperatur und der Reaktionsgeschwindigkeitskonstante für die alkalische Spaltung, einer sehr langsamen Abbaureaktion der Cellulose, zu erhalten. Die löslichen Reaktionsprodukte wurden in ihrer Zusammensetzung auf die Konzentrationen der beiden Diastereomere der Isosaccharinsäure mittels Anionenaustauschchromatographie kombiniert mit gepulster amperometrischer Detektion (HPAEC-PAD), auf die Konzentrationen anderer kurzkettiger aliphatischer Carbonsäuren mittels Ionenausschlusschromatographie (HPIEC), sowie auf die totale Konzentration von organischem Kohlenstoff untersucht. In den unlöslichen Rückständen der Cellulose wurde die Kettenlänge durch Messung des Polymerisationsgrades ermittelt. Der Abbaugrad der Cellulose als Funktion der Reaktionszeit wurde aufgrund der Resultate der Kohlenstoffmessung, sowie des Gewichts der unlöslichen Rückstände berechnet.

Der beobachtete Abbau der Cellulose kann in drei Reaktionsphasen unterteilt werden: (i) eine sehr schnelle Anfangsphase von wenigen Tagen, (ii) eine langsamere Weiterreaktion über einen Zeitraum von ca. 100 Tagen und (iii) ein vollständiger Reaktionsstop nach Abbau von ca. 60 % der anfänglich vorhandenen Cellulosemenge. Diese experimentellen Befunde überraschen in doppelter Hinsicht: Der Abbaugrad als Funktion der Reaktionszeit unterscheidet sich nur unmerklich zwischen (i) den Experimenten bei 60 °C und jenen bei 90 °C und (ii) zwischen reiner Cellulose und Baumwolle. Als Konsequenz davon kann das Abbauverhalten dieser Materialien im untersuchten Temperaturbereich nicht im Rahmen des klassischen Reaktionsschemas einer Kombination des schnellen Abspaltens endständiger Glucoseeinheiten („Peeling-off Prozess") und der langsamen alkalischen Spaltung beschrieben werden. Im Hinblick auf die vorhandenen Inkonsistenzen liegt der Schluss nahe, dass die alkalische Spaltung im Endeffekt gar nicht beobachtet werden konnte. Allerdings reichen die Kenntnisse über den „Peeling-off Prozess" auch nicht aus, um insbesondere den weitgehenden Abbau im Fall von Baumwolle ausreichend zu erklären; dieser müsste folglich über einen bisher nicht beschriebenen Reaktionsweg erfolgen. Massenbilanzen für Kohlenstoff zeigen, dass die Abbaureaktion weitestgehend mit der Bildung von Isosaccharinsäure und anderen kurzkettigen Carbonsäuren beschrieben werden kann.

Im Hinblick auf Vorhersagen zum langfristigen Abbauverhalten von Cellulose bei Raumtemperatur lässt sich die Schlussfolgerung ziehen, dass die von PAVASARS (Linköping Studies in Art and Science, Linköping Universität, Schweden, 1999) vorgeschlagenen Reaktionsgeschwindigkeitskonstanten für die alkalische Spaltung zu hoch sind und dass ein vollständiger Abbau von Cellulose bei diesen Temperaturen nur in einem Zeitbereich von mehreren hundert Jahren erfolgen kann. Allerdings ist es aufgrund der Resultate nicht möglich, die Gültigkeit der linearen Extrapolation („Arrhenius Beziehung") von Reaktionsgeschwindigkeiten, welche bei Temperaturen zwischen 140 und 190 °C gemessen worden waren, auf Raumtemperatur zu erhärten. Unter diesen Gegebenheiten würde der vollständige alkalische Abbau von Cellulose Millionen von Jahren erfordern.

Eine interessante Beobachtung im Rahmen der durchgeführten Experimente ist die chemische Reaktivität der α-Isosaccharinsäure bei 90 °C, welche hypothetisch mit einer Fragmentierung interpretiert wird, die durch Sorption von α-Isosaccharinsäure auf $Ca(OH)_2$ induziert wird. Massenbilanzen für Kohlenstoff zeigen, dass die α-Isosaccharinsäure hierbei in andere kurzkettige Carbonsäuren umgewandelt wird. Eine solche Reaktion wäre im Hinblick auf die Sicherheit für die geologische Tiefenlagerung cellulosehaltiger radioaktiver Abfälle insofern von Interesse, als sie die Konzentration stark komplexierender organischer Verbindung herabsetzen könnte.

RESUME

La dégradation de la cellulose pure (Aldrich) et la cellulose de coton dans une eau interstitielle de ciment artificiel (pH 13.3) a été mesurée à 60 °C et 90 °C sur une durée comprise entre 1 et 2 ans. Le but de l'expérience est d'établir une relation fiable entre les constantes de vitesse de réaction pour l'hydrolyse alcaline de la cellulose (clivage mi-chaîne) qui est une réaction lente, et la température. On a analysé les produits de réaction formés dans la solution pour déterminer (i) la concentration des deux diastéréoisomères d'acide isosaccharinique en utilisant la chromatographie par échange d'anions à haute performance combinée avec la détection ampérométrique pulsée (CEAHP-DAP), (ii) la concentration des acides carboxyliques aliphatiques de faible poids moléculaire, en utilisant la chromatographie par exclusion d'ions à haute performance (CEIHP) et (iii) la concentration totale de carbone organique. On a ensuite analysé les résidus solides de cellulose pour déterminer leur poids sec et leur degré de polymérisation. Le degré de dégradation de la cellulose en fonction du temps de réaction a été calculé sur la base du carbone organique total et du poids sec des résidus de cellulose.

Les expériences sur la dégradation de la cellulose ont permis d'observer trois phases de réaction: (i) une première phase rapide s'étendant sur quelques jours, (ii) une réaction lente se déroulant sur ~100 jours et (iii) un arrêt complet de la réaction après la dégradation de ~60 % du volume initial. Les degrés de dégradation de la cellulose observés en fonction du temps ont été, de manière surprenante, presque identiques pour (i) les expériences réalisées à 60 °C et 90 °C et (ii) pour la cellulose pure et la cellulose de coton. On peut en conclure que le comportement des matériaux testés à ces températures ne peut pas être expliqué selon le schéma de réaction classique alliant un processus d'épluchage rapide (peeling-off) à l'hydrolyse alcaline lente. On peut supposer que l'hydrolyse alcaline n'a même pas pu être observée lors des expériences. Cependant, si cette hypothèse est exacte, cela signifie que la dégradation de la cellulose se déroule par l'intermédiaire d'un autre type de réaction inconnu. Les bilans de masse pour le carbone montrent que la grande majorité des produits de réaction identifiés dans la solution peuvent être mis en rapport avec la formation d'acides isosacchariniques et d'autres acides carboxyliques à faible poids moléculaire.

En ce qui concerne les prédictions à long terme pour la dégradation de cellulose à la température ambiante, on peut conclure que les constantes de vitesse de réaction pour l'hydrolyse alcaline proposées dans PAVASARS (*Linköping Studies in Arts and*

Science, 196, Linköping University, Sweden, 1999) sont trop élevées. Selon cette étude, la dégradation complète de la cellulose à ces températures interviendrait en l'espace de quelques centaines d'années. Toutefois, les expériences effectuées ne permettent pas de confirmer que les vitesses de réaction à température ambiante pourraient être déduites, par le biais d'une extrapolation linéaire ("équation d'Arrhenius"), des vitesses de réaction mesurées à des températures comprises entre ~140 et 190 °C – ce qui fait passer à plusieurs millions d'années la durée nécessaire à la dégradation complète de la cellulose.

Lors des expériences effectuées, on a en outre observé une instabilité d'acide α-isosaccharinique à 90 °C. A cet égard, on peut formuler l'hypothèse d'une fragmentation provoquée par la sorption d'acide α-isosaccharinique sur $Ca(OH)_2$. Les bilans de masse de carbone ont montré que l'acide α-isosaccharinique est, de ce fait, transformé aux acides carboxyliques à faible poids moléculaire. Au regard de l'évaluation de la performance à long terme du stockage définitif des déchets radioactifs contenant de la cellulose, il s'agit là d'une propriété intéressante dans la mesure où elle permettrait de réduire la concentration des agents organiques complexants.

1   INTRODUCTION

1.1   Impact of the degree of cellulose degradation

The degree of cellulose degradation is a key parameter in the assessment of the effect of strong complexants being formed via alkaline cellulose degradation on the speciation and mobility of radionuclides in a repository for radioactive waste. Fig. 1 shows the prediction of the concentration of isosaccharinic acid[1] (ISA), the main product of anaerobic cellulose degradation formed at room temperature (VAN LOON & GLAUS, 1998) as a function of the degree of cellulose degradation (*Celdeg*). The parameters used for this calculation are taken from VAN LOON & GLAUS (1998) and are representative for a type of cellulose-containing waste to be disposed of in a repository for low- and intermediate level radioactive waste. Fig. 1 illustrates that the connexion between *Celdeg* and concentration of ISA is strongly non-linear. The reason for this behaviour can be found in the strong sorption of ISA on cement (VAN LOON et al.,
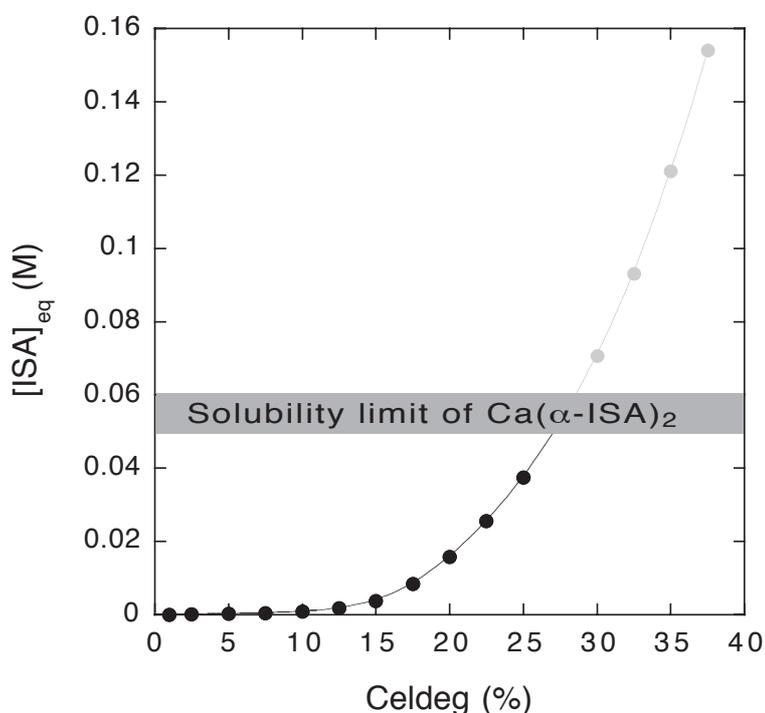
Fig. 1:

Prediction of pore water concentration of isosaccharinic acid (ISA) for typical conditions encountered in a cementitious repository for radioactive waste planned in Switzerland. The model calculations are based on parameters for cellulose degradation and sorption of ISA on cement according to VAN LOON & GLAUS (1998) and VAN LOON et al. (1997). In the presence of Ca^{2+} ions the solubility of α-ISA cannot exceed the limit indicated by the gray bar.

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[1] Isosaccharinic acid is a general term for 3-deoxy-2-C-(hydroxymethyl)-D-aldonic acids. In the present report the term isosaccharinic acid is used for simplicity for the glucoisosaccharinic acids. Note that these names are in plural because several stereoisomeric forms may exist.

1997). At relatively low degrees of cellulose degradation, the sorption of ISA on cement is responsible for the low concentrations of ISA in cement pore water. At large degrees of cellulose degradation, the amount of ISA formed is such that the sorption capacity of cement is exceeded, resulting in a sharp increase of ISA concentration in cement pore water until the solubility limit of $Ca(\alpha\text{-ISA})_2$ is reached[2]. Concentrations of ISA of the order of higher millimolar may have strong effects on the sorption of critical radionuclides, such as trivalent and tetravalent lanthanides and actinides (VAN LOON et al., 1999). For this reason the prediction of the degree of cellulose degradation is a crucial step in the assessment of the effect of alkaline cellulose degradation on the speciation and mobility of radionuclides in a cementitious repository for radioactive waste. Knowledge on the kinetics of cellulose degradation is a necessary prerequisite for such predictions.

1.2   The alkaline degradation of cellulose

Information on structural features of cellulose and its chemistry can be found in many places (WHISTLER & BEMILLER, 1958; KRÄSSIG, 1985; OKAMURA, 1991; LAI, 1991; GREENFIELD et al., 1993; KNILL & KENNEDY, 2003). An overview specifically related to the needs of safe disposal of radioactive waste is given by VAN LOON & GLAUS (1998). Briefly, the anaerobic degradation of cellulose at alkaline conditions is governed by three main processes (cf. Fig. 2): (i) the endwise clipping of glucose units through the 'peeling-off process', induced by a nucleophile addition of hydroxide ions to reducing end groups (latent aldehydes), (ii) mid-chain scissions of the cellulose chain, referred to in the following as 'alkaline hydrolysis', induced by stochastic deprotonation of glucose subunits at any place of the cellulose chain, and (iii) formation of non-reacting end groups through chemical transformation of reducing end groups to metasaccharinate, which stops the peeling-off process. In addition the possible degradation of cellulose via the peeling-off process can be prevented owing to the presence of reducing end groups in crystalline regions of the cellulose molecule, where they are not accessible to the attack of hydroxide ions. Note that the pathways shown in Fig. 2 are a simplification of the complexity of reaction products found in reality.

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[2] The solubility limit given in Fig. 1 is based on experimentally observed concentrations of α-ISA in artificial cement pore water (VERCAMMEN 2000), which are larger by a factor of ~2 than model predictions for the corresponding systems (VERCAMMEN et al., 1999).
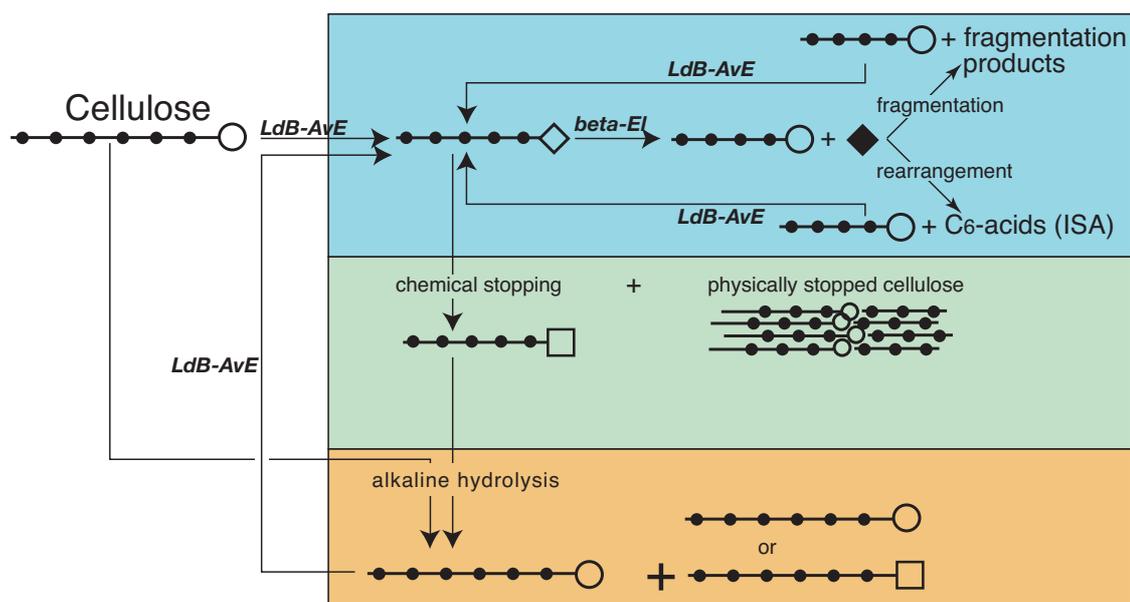
Fig. 2:

Simplified representation of the processes involved in the alkaline degradation of cellulose. Note that the chain lengths depicted are not represented to scale and do not indicate changes in chain-length due to progression of the reactions. The blue rectangle refers to the peeling-off process, the green rectangle to stopping processes and the brown rectangle to the alkaline hydrolysis.

Structural elements:

● *glucose monomeric unit*
○ *reducing end-group (aldehyde functional group)*
□ *chemically stopped end-group (metasaccharinic acid or others)*
◇ *activated end-group (enolate functional group)*
◆ *intermediate product (4-deoxy-2,3-hexodiulose)*

Reactions:

LdB-AvE   Lobry de Bruyn – Alberda van Ekenstein transformation

beta-El   β-Elimination

Depending on ionic composition of the reaction solution, temperature, atmosphere and reaction time, a variety of fragmentation products, such as C_1-, C_2- or C_3 carboxylic acids (for an overview, see NIEMELÄ, 1990) may be formed from the *intermediate product* (4-deoxy-2,3-hexodiulose). Further alternative pathways starting from the *intermediate product* — not shown in Fig. 2 — may lead to the formation of anhydroisosaccharinic acid (PETERSSON & SAMUELSON, 1976) or C_4-, C_5- and C_6- mono- and dicarboxylic acids (ALFREDSSON & SAMUELSON, 1968; LÖWENDAHL et al., 1976). Chemical stopping may also lead to the formation of other end-groups than metasaccharinic acid (MSA), as has been shown by JOHANSSON & SAMUELSON (1974).

Alkaline hydrolysis leads to the reformation of a reducing end group, whereby the peeling-off process can be started again. For this reason both the peeling-of process and the alkaline hydrolysis lead to the formation of ISA, which is actually a mixture of α-isosaccharinic acid (**1**, abbreviated as α-ISA) and β-isosaccharinic acid (**2**, abb-

reviated as β-ISA). A further consequence of this circumstance is that alkaline hydrolysis cannot be studied separately from the peeling-off process.

COOH
|
HOH₂C—C—OH
|
CH₂
|
H—C—OH
|
CH₂OH

1

COOH
|
HO—C—CH₂OH
|
CH₂
|
H—C—OH
|
CH₂OH

2
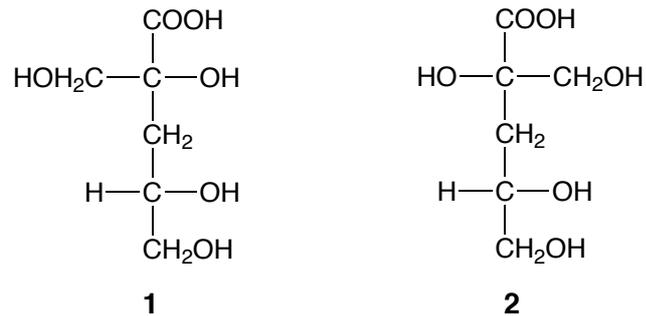
The degradation of cellulose due to the peeling-off process is described by the following empiric equation (VAN LOON & GLAUS, 1998):

$$(Celdeg)_t = 100 \cdot \frac{k_1}{k_t} \cdot (G_r)_0 \cdot (1 - e^{-k_t \cdot t})$$ (1)

Note that, in this report, *Celdeg* is expressed as a percentage of the total amount of cellulose, throughout. k_1 and k_t are first order reaction rate constants involved in the peeling-off process and $(G_r)_0$ is the mole fraction of reducing end groups initially available. $(G_r)_0$ can be related approximately to the degree of polymerisation of the cellulose chain (*DP*) by the following equation:

$$(G_r)_0 = \frac{1}{DP}$$ (2)

The alkaline hydrolysis of cellulose has been described by the following first order kinetic equation (FRANZON & SAMUELSON, 1957):

$$\ln(Y) = -k \cdot t$$ (3)

where *Y* is the fraction of unreacted cellulose and *k* a first-order reaction rate constant associated to the alkaline degradation of cellulose.

VAN LOON & GLAUS (1998) proposed a kinetic expression comprising cellulose degradation both via the peeling-off process and the alkaline hydrolysis:

$$(Celdeg)_t = 100 - 100 \cdot \left(\frac{1 - \frac{k_1}{k_t} \cdot (G_r)_0 \cdot \left(1 - e^{-k_t \cdot t}\right)}{e^{k \cdot t}} \right)$$ (4)

Note that this equation is valid for the case, where the peeling-off process is much faster than the alkaline hydrolysis, which is actually the case.

1.3   Conflicting long-term predictions for cellulose degradation

Conflicting views exist on the question of how much time is needed for cellulose to be degraded in a cementitious repository for radioactive waste (VAN LOON & GLAUS, 1997; PAVASARS, 1999; ASKARIEH et al., 2000; KNILL & KENNEDY, 2003). Experimental data have been evaluated in "long-term" experiments in a research group at Linköping University in Sweden (PAVASARS, 1999) and in one research group at the Paul Scherrer Institut, Switzerland (VAN LOON & GLAUS, 1998). The boundary conditions used in both studies have been the same. Experiments were carried out under exclusion of air at 25 ±2°C in artificial cement pore water simulating the first stage of cement degradation with respect to the concentrations of Na^+, K^+ and Ca^{2+} (BERNER 1990). pH was kept at ~13.3 throughout the degradation time investigated. In both cases the same starting material, Aldrich Cellulose, has been used at comparable solid to liquid ratios (100 g·dm^{-3}; 5 or 10 g·dm^{-3}, respectively). Surprisingly, the long-term predictions for cellulose degradation made in these studies are not the same. Whereas the Swedish group predicts complete degradation within ~100 years (PAVASARS 1999), the Swiss group concludes that after this time only small proportions of cellulose (of the order of 5 –10 %) will be degraded and that complete degradation of cellulose will take between 10^5 and 10^7 years (VAN LOON & GLAUS, 1997; VAN LOON & GLAUS, 1998) at 25 °C[3]. In the following, possible reasons for this discrepancy are worked out. In a first step, the results of both studies are compared based on the experimental raw data, and in a second step the ways to determine the reaction rate constants are compared.

As is shown in Fig. 3, the raw data — i.e. the concentration of total dissolved organic carbon (TOC) and ISA — are in fairly good agreement. The concentration of ISA was measured by capillary zone electrophoresis (CZE) in the Swedish group and by high performance anion exchange chromatography (HPAEC) in the Swiss group. CZE allows only for determination of the sum of α-ISA + β-ISA, whereas these diastereomers can be discriminated and determined separately by HPAEC. Both datasets can be interpreted as indicating that cellulose degradation through the peeling-off reaction has come to an end. However, with respect to long-time scales, the

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[3] Predictions from Nirex (ASKARIEH et al., 2000) which are based on experiments carried out — on a shorter time scale and at pH ~12.5 — by AEA Technology, Harwell, lie somewhere between these extreme cases. Their findings are explained by the existence of different regions in cellulose with different crystallinity and different accessibility towards hydroxide ions.
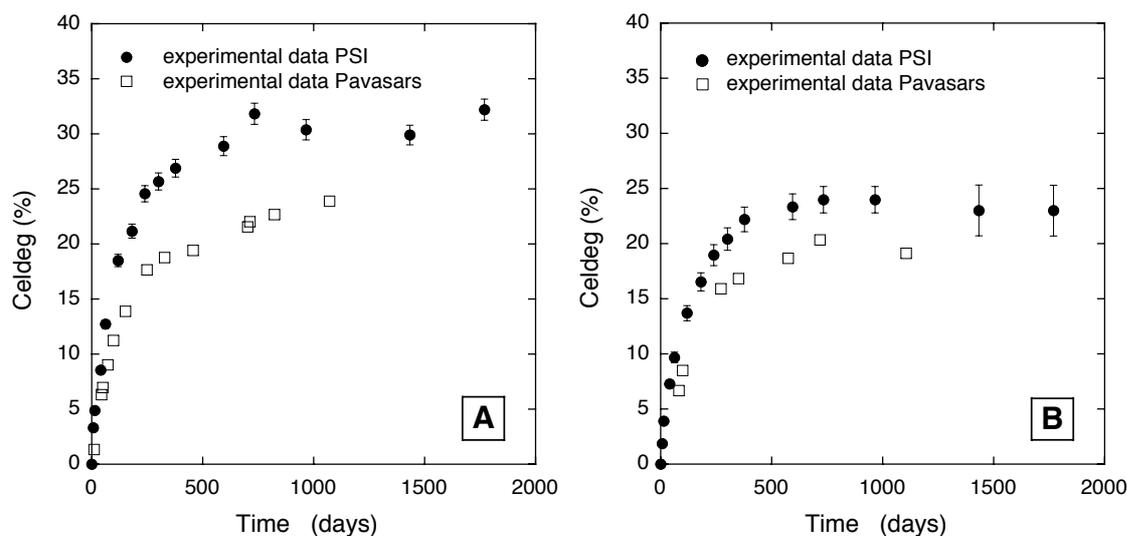
Fig. 3:

Comparison of Celdeg calculated from TOC (plot A) and [ISA] (plot B) for degradation experiments carried out at pH 13.3 and at 100 g·dm^{-3} of cellulose. No experimental uncertainty was assigned to the data of PAVASARS (1999).

data of PAVASARS (1999) based on TOC measurement do not clearly exclude the possibility that degradation of cellulose is still continuing via a slow process. For this unclear situation, the authors of both groups come to completely different conclusions concerning the long-term behaviour of cellulose in a cementitious repository for radioactive waste.

The question, whether or not, alkaline degradation of cellulose proceeds only to a limited extent within the order of ~10^5 years, depends — besides the type of kinetics involved — on the value used for the reaction rate constant for the alkaline hydrolysis. It is thus the use of different methods to evaluate this constant, which is obviously responsible for the different conclusions drawn in the work of PAVASARS (1999) and VAN LOON & GLAUS (1998).

- PAVASARS (1999):

  PAVASARS fitted his data (cf. Fig. 3) directly to eqn. (4). The corresponding fit is shown in Fig. 4 as solid line. A critical assessment of the value for k proposed by PAVASARS ($k = 3 \cdot 10^{-6}$ h^{-1}) however, shows that a variety of other numerical values could as well explain the experimental data within the range of their uncertainty. As is shown in Fig. 4 by the dotted line, this range may cover values from completely different orders of magnitude, such as $8.6 \cdot 10^{-11}$ h^{-1} (the value for k proposed by VAN LOON & GLAUS, 1998). Even the complete absence of alkaline hydrolysis reaction would result in the same curve as calculated for $k = 8.6 \cdot 10^{-11}$ h^{-1}. From a statistical
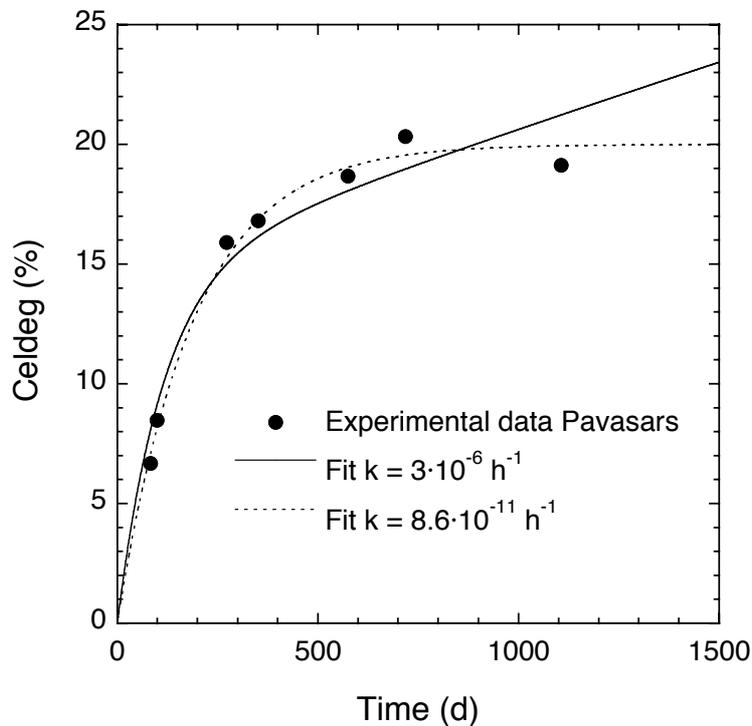
Fig. 4:
Different ways to model the ISA data shown in Fig. 3. The solid and dotted lines are based on a model including alkaline hydrolysis, but using different reaction rate constants k.

point of view and based on the data available, none of the models shown in Fig. 4 can be clearly preferred over the other, meaning that the error function has not a clearly defined minimum. Note that the data shown in Fig. 4 are chosen arbitrarily from the 4 datasets given in Fig. 3. For the TOC data of PAVASARS (1999), a somewhat clearer trend to a slight increase in concentration on longer incubation times can be stated, however this dataset cannot change the overall impression given by the 4 datasets. It has further to be noted that the data given by the Swiss group cover a noticeable longer time period than those provided by PAVASARS (1999) (cf. Fig. 3).

• VAN LOON & GLAUS (1998):

VAN LOON & GLAUS noted that it is not possible to derive a reliable value for k from their data measured at room temperature. For this reason, the value of k at room temperature has been extrapolated from data measured at temperatures between 146 °C and 187 °C using the Arrhenius equation. The reliability of this extrapolation procedure may be affected by statistical and systematic uncertainties. The statistical uncertainties can be mathematically handled and lead to an uncertainty of k of approximately one order of magnitude. In contrast, the systematical uncertainties cannot easily be bound. The extrapolation implies that the Arrhenius

equation is valid across the whole range of temperatures between 187 °C and room temperature. This hypothesis cannot be proven *a priori*, because *k* is an overall constant for the superposition of a sequence of different elementary reaction steps. However, at the moment, there is no better alternative than doing such an extrapolation.

1.4   Purpose and strategy followed in the present study

All these considerations show that the selection of a reasonable value for *k* valid for room temperature needs additional experiments. Neither the data of PAVASARS (1999) nor those of VAN LOON & GLAUS (1998) allow for an accurate estimate to be made. As is shown in Fig. 5, it is only of restricted use to run the current experiments for longer times. Fig. 5 shows that, for an observation time of 10 years, *k* needs to be of the order of 10^{-5} h^{-1}, in order that a significant (let's say at least by 20 %) increase in ISA concentration may be observed in the time between ~2 and 10 years. This means that a value for *k* as proposed by VAN LOON & GLAUS (1998) cannot be corroborated by such experiments. Only for the case that a value of the order of the one proposed by PAVASARS (1999) is correct, a time span of 10 years is sufficient.

For this reason, additional experimental data obtained from experiments at elevated temperature are required, which is the purpose of the present study. The purpose of additional experiments is twofold: (i) Discrimination of possible kinetic models for the
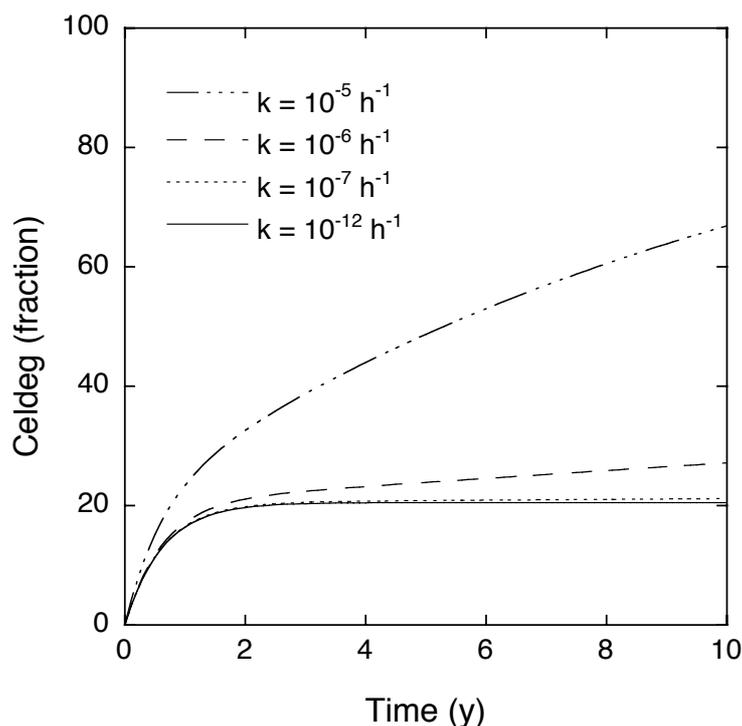
Fig. 5:

Cellulose degradation simulated using different values for the kinetic constant for alkaline hydrolysis k.

degradation of cellulose and (ii) determination of the reaction rate constants involved. The line followed by the experiments presented in this work is mainly to test, whether or not extrapolation of the reaction rate constant for alkaline hydrolysis of cellulose, as proposed by VAN LOON & GLAUS (1998) is correct. Note that alkaline hydrolysis was monitored in the past by measuring the decrease in the degree of polymerisation and weight loss of the remaining solid. According to the current theories, all degradation products are transformed to α-ISA or β-ISA as the main products. However, such quantitative formation of ISA has not been directly shown yet. Through the specific analysis of α-ISA and β-ISA by HPAEC in the proposed experiments, this point can be unequivocally clarified. With respect to the needs of safety analysis, not only the reaction rate constant for alkaline hydrolysis is of interest, but also the nature of the degradation products with respect to complexation of safety relevant radionuclides. In the case that cellulose degradation reaches completeness at high temperatures within short time, also the complexing ability of the degradation products needs to be investigated, if other degradation products than α-ISA or β-ISA are formed.

The following considerations show, how experiments at elevated temperature have to be designed in order that different kinetic models can be discriminated from each other as well as possible. 3 feasible scenarios for the reaction rate constants and their temperature dependence are discussed in the following. The scenarios are summarised in Fig. 6. Note that the sequence of the scenarios has no relevance to
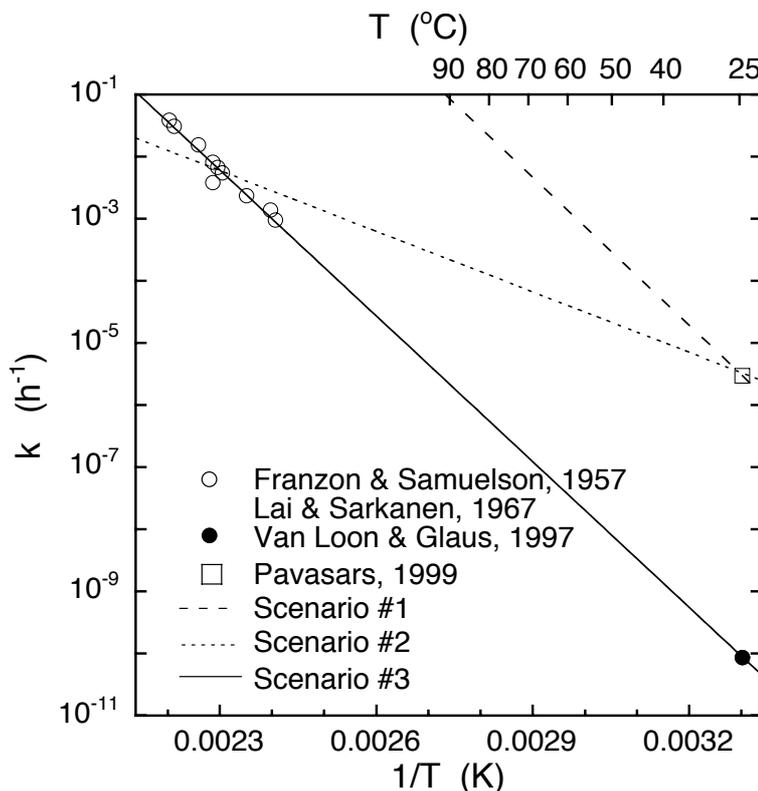
Fig. 6:
Different scenarios by which the data in the literature may be explained. For details, the reader is referred to the text.

their probability of being correct.

Scenario #1: The value for k proposed by PAVASARS (1999) is correct, while incompatible with the data measured earlier (FRANZON and SAMUELSON, 1957; LAI and SARKANEN, 1967). However, the temperature dependence of the kinetic constants is correctly reflected by the latter data and follows an Arrhenius type equation.

Scenario #2: The value for k proposed by PAVASARS (1999) is correct, while compatible with the data measured earlier (FRANZON and SAMUELSON, 1957; LAI and SARKANEN, 1967). The temperature dependence of k is described by an Arrhenius equation, which is forced through the value proposed by PAVASARS (1999). Consequently, the values measured earlier (FRANZON and SAMUELSON, 1957; LAI and SARKANEN, 1967) are correct within their order of magnitude, but significant deviations from the true values have to be tolerated.

Scenario #3: The values measured earlier (FRANZON and SAMUELSON, 1957; LAI and SARKANEN, 1967) and the extrapolation to room temperature proposed by VAN LOON & GLAUS (1998) are correct. The value proposed by PAVASARS (1999) is an artefact due to the enormous uncertainties in the determination of the minimum of the error function.

The temperature in the new experiments needs to be chosen such that, on the one hand, the results can be obtained within a reasonable time, and on the other hand, the range of data available for extrapolation will be significantly broadened by the new experiments. From such considerations it has been decided to carry out the new experiments at temperatures of 60 °C and 90 °C. The predictions for each of the scenarios based on temperatures of 25°C, 60°C, and 90°C are shown in Fig. 7 for Aldrich cellulose. The calculations are based on eqn. (4) using values for k taken from Fig. 6 and values for k_1 and k_t based on the Arrhenius parameters given by VAN LOON & GLAUS (1998). Note that the degree of cellulose degradation due to the peeling-off process levels off at different values for different temperatures. The explanation for this phenomenon can be found in different dependencies of the reaction rates involved (k_1, k_t, cf. eqn. (1)) on temperature.
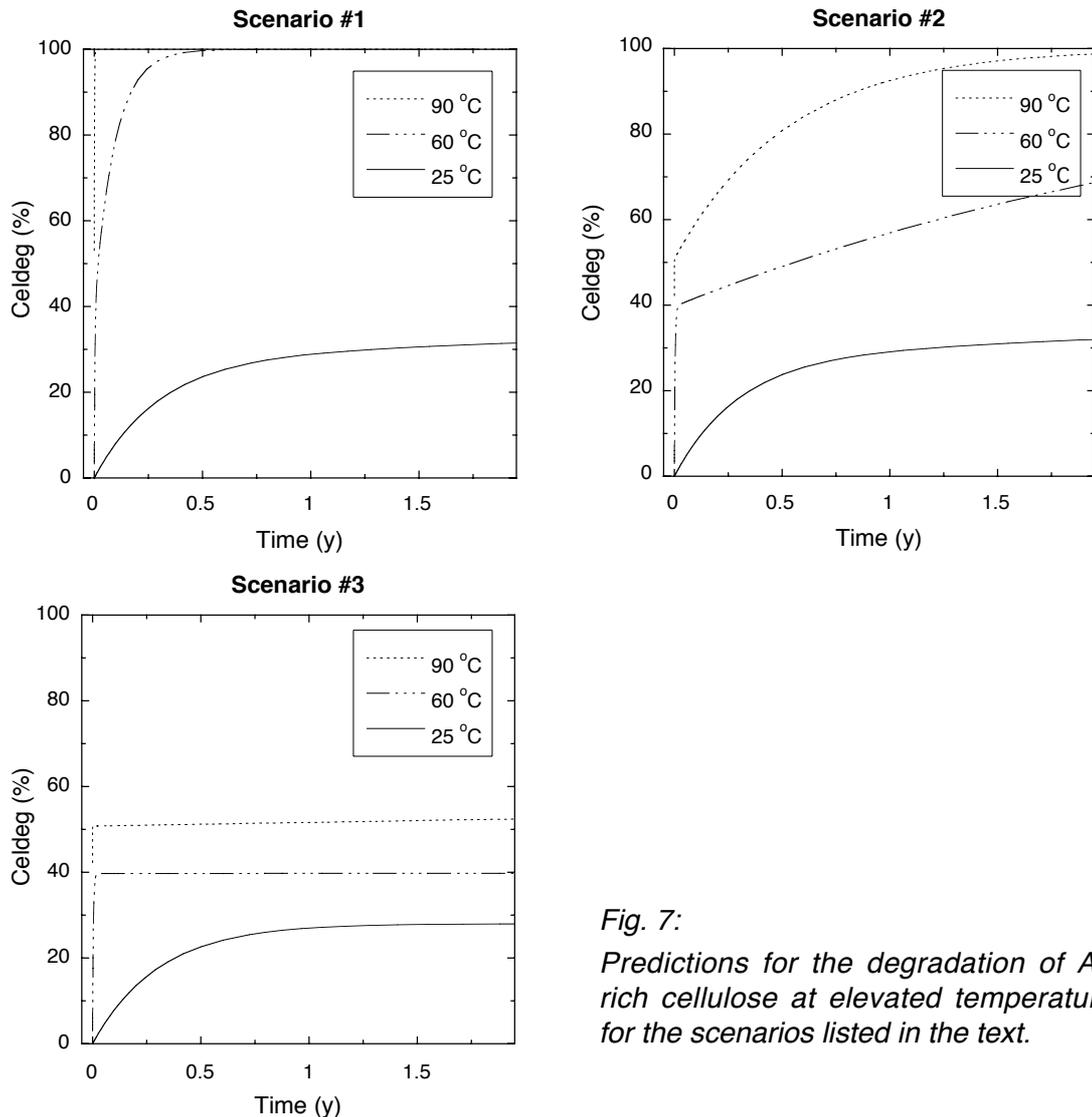
Fig. 7:

Predictions for the degradation of Ald-rich cellulose at elevated temperatures for the scenarios listed in the text.

The interpretation of the results will not in all cases be an easy task. If, on the one hand, complete degradation of cellulose is observed within a short time, it is clear that the idea of the partial stability of cellulose over thousands of years has to be abandoned. If, on the other hand, cellulose is degraded only partially at 90 °C within two years, a situation based on scenario #3 will be the most probable interpretation. However, the discrimination of different degradation models has always to be done in view of the analytical uncertainties involved in the determination of reactant and product concentrations. A reaction proceeding very slowly may be interpreted as being in equilibrium state and vice versa, if the observation time is too short and the analytical uncertainties exceed the actual increments of concentration in-/decrease. Further note that reaction kinetics as shown for scenario #2 (60 °C and 90 °C) can be interpreted equally in two ways, if only based on *Celdeg* measured as a function of time:

- One reactant involved in two reactions with different reaction rate constants, e.g. amorphous cellulose reacting via peeling-off and alkaline hydrolysis pathway as proposed by VAN LOON & GLAUS (1997).

- Two reactants in different states of aggregation (or having different accessibility) reacting via the same pathway, e.g. crystalline and amorphous cellulose reacting via peeling-off reaction as proposed by ASKARIEH et al. (2000).

For this situation it is important to have independent information about the products formed, such as the degree of polymerisation. In the first case, the degree of polymerisation is expected to decrease much more rapidly than in the second case. Further, it is necessary to consider the data in their whole context (i.e. data evaluated within a series of temperatures) instead of picking out single data points that may have been affected by possible analytical artefacts.

In the case of Aldrich cellulose the information obtained from measurements of the degree of polymerisation may possibly be of secondary importance. Aldrich Cellulose has a degree of polymerisation of ~120. From a conceptual point of view, approximately half of the glucose units available will be peeled-off, if the model proposed by FRANZON & SAMUELSON (1957) (i.e. average number of glucose units peeled-off: 65) is correct. Consequently, if chain-scission reactions still proceed after the initial peeling-phase, a relatively rapid dissolution of the whole amount of Aldrich cellulose is expected. It would not be possible to discriminate such a reaction from kinetics involving peeling-off only. In the case of cotton cellulose, on the contrary, such a scenario cannot be expected owing to the large degree of polymerisation (~1700, measured in this work). From these considerations, the combined information gained from Aldrich cellulose and from cotton will probably have a larger weight than the one gained from one type of cellulose only.

Summary of the objectives:

The purpose of the experiments is to establish a reliable relationship between temperature and the reaction rate constant for the alkaline hydrolysis (mid-chain scission) of cellulose by:

- Discrimination of possible kinetic models for the degradation of cellulose.

- Determination of the reaction rate constants involved.

2   EXPERIMENTAL

Artificial cement pore water (denoted to as ACW-I in the following), a Ca saturated solution of NaOH and KOH, was prepared according to VAN LOON & GLAUS (1998). The calcium salt of α-isosaccharinic acid (α-ISA) and solutions of β-isosaccharinic acid (β-ISA) were synthesised according to GLAUS et al. (1999). The same cellulose materials as described in VAN LOON & GLAUS (1998), viz. powdered cellulose (Aldrich cellulose powder, 20 μm spheres, art. 31,069-7) and cotton cellulose (Migros, Switzerland) were used for the present experiments. Mixtures of cellulose and $Ca(OH)_2$ in ACW-I were prepared in thick-wall Teflon containers (Semadeni, Switzerland) by weighing the solids and adding argon-flushed ACW-I heated before to 60 or 90 °C. All steps were carried out under flushing of argon gas in order to avoid excessive contact of the suspensions with air. The vessels were stored in an oven at 60 ±2 or 90 ±2 °C. According to the concentrations of NaOH and KOH, the initial pH was of the order of 13.3 and decreased gradually with increasing reaction time as shown later on (cf. section 3). The colour of the solution phases of the systems with Aldrich cellulose changed within a few days to brownish, whereas the systems containing cotton cellulose remained colourless. An overview of the various experimental systems is given in Tables 1a and 1b. Owing to the homogeneity of powdered cellulose suspensions with respect to the distribution of the solid, the experiments with Aldrich cellulose were set up as "single-batch experiments", in which a series of samples were taken from the same batch after the desired reaction times. In contrast, the experiments with cotton cellulose were set up as "multiple-batch experiments", in which a series of identical systems was prepared, and the complete batch was used for the analyses performed at a single reaction time.

For the analysis of organic compounds present in the solution phase of single-batch experiments, aliquots of these mixtures were taken after a given contact time under flushing with argon gas and filtered while hot through 0.2 μm membrane filters (nylon, Schleicher & Schuell, Germany), after discarding the first millilitre. The evaporation of water during the storage of the samples in the oven was followed by weighing the containers before and after sampling. A slight, but measurable leakage of the Teflon containers and the evaporation during the opening and flushing of the containers are the two reasons for water evaporation. For the analysis of the insoluble cellulose fraction, the filter residue was washed with water until pH < 9 in order to remove $Ca(OH)_2$ and subsequently dried under vacuum at 40 °C. The filtrates used for the analyses were kept in a refrigerator at –20 °C.

Tab. 1a:　　　Overview of cellulose degradation experiments carried out at 90 °C.

Sample name	Type of cellulose	Cellulose / ACW-I ($g \cdot dm^{-3}$)	S : L^a ($g \cdot dm^{-3}$)	Start	Duration (months)	Type of experiment	Purpose/remarks
A90-1 A90-2 A90-3	Aldrich^b	10	1	Feb. 2001	22	Single-batch	Main experiment for Aldrich cellulose
A90-4 A90-5	Aldrich^b	10 10	1 1	March 2001	7	Single-batch	Diluted 1:5 after 60 days Diluted 1:20 after 60 days
A90-6 A90-7	Aldrich^b	2 0.5	1 1	May 2001	5	Single-batch	Reference for A90-4/5
B90-1	Aldrich^b	10	—	Feb. 2001	22	Single-batch	No Ca(OH)$_2$ added
C90-1 ...-6	Aldrich^b	10	1	Feb. 2001	13	Multiple-batch	Measurement of dry weights remaining
D90-1	—	—	1	Feb. 2001	22	Single-batch	"blank" (no cellulose)
E90-1 ...-16	Cotton^c	10	1	Feb. 2001	21	Multiple-batch	Main experiment for cotton
F90-1 ...-7	Cotton^c	10	—	Feb. 2001	21	Multiple-batch	No Ca(OH)$_2$ added
G90-1 ...-6	Cotton^c	60	1	May 2001	11	Multiple-batch	Effect of increased amount of cellulose

^{a} Ratio of Ca(OH)$_2$: ACW-I　　　^{b} DP of ~120 (measured value)　　　^{c} DP of ~1800 (measured value)

Tab. 1b: Overview of cellulose degradation experiments carried out at 60 °C.

Sample names	Type of cellulose	Cellulose / ACW-I (g·dm⁻³)	S:L[a] (g·dm⁻³)	Start	Duration (months)	Type of experiment	Purpose/remarks
A60-1	Aldrich[b]	10	1	Feb. 2002	3	Single-batch	Aborted after 3 months (malfunction of oven)
A60-2	Aldrich[b]	10	1	Jun. 2002	8	Single-batch	Main experiment for Aldrich cellulose
C90-1 ...-11	Aldrich[b]	10	1	Feb. 2002	12	Multiple-batch	Measurement of dry weights remaining
D60-1	—	—	1	Feb. 2002	12	Single-batch	"Blank" (no cellulose)
E90-1 ...-18	Cotton[c]	10	1	Feb. 2001	12	Multiple-batch	Main experiment for cotton

[a] Ratio of $Ca(OH)_2$: ACW-I   [b] DP of ∼120 (measured value)   [c] DP of ∼1700 (measured value)

The high performance anion exchange chromatography (HPAEC) system using a CarboPac PA-100® column (Dionex, Switzerland) to measure the concentrations of α-ISA and β-ISA as well as the preparation of standard solutions of these compounds has been described elsewhere (GLAUS et al., 1999). MSA was only tentatively identified based on co-elution with a reference compound synthesised in our laboratory. The signal response of the detection of MSA is larger by a factor of ~50 than the response for ISA. For this reason the concentrations of MSA are not significant as compared to the concentration of the ISA isomers, and a quantitative evaluation of the peaks tentatively identified as MSA was not carried out. The samples were diluted with water by a factor of at least 10, in order to avoid matrix effects caused by excessive hydroxide concentrations present in the samples injected. The same reference can be consulted for the high performance ion exclusion chromatography (HPIEC) measurements using an IonPac ICE-AS6® (Dionex, Switzerland) to measure short chain aliphatic carboxylic acids (commercial products of acetic-, formic-, glycolic and lactic acid). The eluent concentration was 0.6 mM heptafluorbutyric acid, separation was carried out at a column temperature of 60 °C. The samples were pretreated using Onguard-H® cartridges (H$^+$-form) in order to remove trace metal ions and to acidify the samples. Representative HPAEC and HPIEC chromatograms are shown in the Appendix.

The concentration of total dissolved organic carbon (TOC) was analysed in a first phase of the experimental programme by a Dohrmann DC-180® Carbon Analyser (Schmidlin, Neuheim, Switzerland) and in a second phase a TOC-V WP® device (Shimadzu, Reinach, Switzerland). Both devices use a UV-promoted persulfate wet oxidation method. A series of test measurements has shown that the results obtained with both devices were identical within the range of experimental uncertainty. The oxidation reagent was a 2 % solution of $K_2S_2O_8$ in 30 mM of H_3PO_4. Calibrations were performed with solutions of potassium hydrogenphthalate as a standard. Alkaline samples were acidified using a suitable amount of H_3PO_4 before analysis.

Na, K, Ca and Si were measured by ICP-OES (Varian, AX-Vista Pro CCD Simultaneous ICP-OES).

The hydroxide concentration was measured by acid-base titration. 30 cm^3 of demineralised water were placed in a titration vessel and purged with N_2 for 15 min. An aliquot of the alkaline degradation solutions or ACW-I was added, and the mixture was purged with N_2 for another two min. The mixture was then titrated automatically with

HCl under an N_2 atmosphere (Titroprocessor 610, Metrohm). The concentration of hydroxide, [OH⁻] (mM), ions was calculated from the following equation:

$$[OH^-] = \frac{V_{EP1} \cdot c_{HCl}}{V_s}$$
(5)

where:

V_{EP1} =   volume of HCl used to titrate the sample to the first endpoint (cm^3)

V_s =   volume of the sample titrated (cm^3)

c_{HCl} =   concentration of HCl (mM)

The degree of cellulose degraded (*Celdeg*) can be calculated based on three different parameters:

(i)   sum of [α-ISA]+[β-ISA]:   —>   *Celdeg*$_{ISA}$ (%)

(ii)   total dissolved carbon in solution (TOC):   —>   *Celdeg*$_{TOC}$ (%)

(iii)   dry weight: —>   *Celdeg*$_{DW}$ (%)

The corresponding analytical expressions are:

$$Celdeg_{ISA} = \left([\alpha - ISA] + [\beta - ISA]\right) \cdot \frac{1}{f_v} \cdot \frac{M_{mono} \cdot V}{w_C \cdot 1000} \cdot 100$$
(6)

where:

f_v =   relative volume concentration due to water evaporation (given as fraction)

V =   volume of ACW-I initially added (cm^3)

W_C =   dry weight of cellulose added (g)

M_{mono} =   relative molar mass of monomer unit of cellulose (162 g·mol⁻¹)

$$Celdeg_{TOC} = \frac{TOC}{1000 \cdot A_C} \cdot \frac{1}{f_v} \cdot \frac{M_{mono} \cdot V}{w_C \cdot 1000 \cdot 6} \cdot 100$$
(7)

where:

TOC =   concentration of total dissolved organic carbon (mg·dm⁻³)

A_c =   atomic weight of carbon (12 g·mol⁻¹)

$$Celdeg_{DW} = 100 \cdot \left(1 - \frac{w_C}{w_C^0}\right)$$
(8)

where:

w_C =   dry weight of cellulose remaining after degradation (g)

w_C^0 =   initial dry weight of cellulose corrected for loss by sampling (g)

The degree of polymerisation (*DP*) was measured viscosimetrically (Atisholz AG, Luterbach, Switzerland). In general the samples were measured in duplicate. For the samples from the Aldrich cellulose degradation series, the results were found to be in reasonable agreement. However, for the samples from the cotton series, differences of 50 to 100 between the two replicate measurements were observed in many cases. This can probably be explained by the heterogeneous composition with respect to *DP* of the degraded cotton cellulose. An empirical estimate of the standard uncertainty for the average *DP* of cotton cellulose samples having *DP* > ~200 would be of the order of ±50 and ± 20 for samples with *DP* < ~200.

The procedure to quantify the experimental uncertainties follows the recommendations given by the EURACHEM Working Group on Uncertainty in Analytical Measurements (WILLIAMS et al., 1995), which is virtually a practical application for analytical chemistry of the recommendations given in the "ISO-Guide" (N.N., 1993). The procedure allows for an integrative treatment of statistical and non-statistical (systematic) errors and briefly consists of the following steps:

1. Identification and specification of the different sources of uncertainty

2. Quantification of the uncertainty increments

3. Calculation of a "combined uncertainty" in the result

4. Reevaluation of the uncertainty increments and recalculation of the combined uncertainty (if necessary)

It would be beyond the scope of this report to trace back the calculation of experimental uncertainties in detail. Just as a guideline, it may be mentioned that the uncertainties of analytical results both obtained for HPAEC and TOC measurements were mainly based on the transformation of signal to concentration using linear calibration functions. Systematic errors were formally allocated to the calibration data in order to be properly included in the evaluation (GLAUS, 2001). The relative experimental uncertainties in ICP-OES measurements are of the order of 5 %. No reliable estimate for the uncertainties in the measurement of degree of polymerisation of cellulose can be made as yet. The experimental uncertainties evaluated in this way have to be looked at as the best possible estimate for the propagation of all known errors. No attempt has been undertaken to make an estimate for unknown errors. Such type of error sources can only be detected by inconsistencies in the results.

3   RESULTS

3.1   Degree of cellulose degraded

The source data for the calculation of the degree of cellulose degraded, i.e. the sum of concentrations of α-ISA and β-ISA[4], TOC, and the weight of unreacted cellulose, are summarised in Tables 2 – 6. These data can be looked at as raw data, although they are the result of mathematical transformations, such as the calibration in the analysis of ISA and TOC. For the sake of simplicity, no experimental uncertainties are specified in these tables. However, they have been assessed for all the analytical data with the exception of *DP*, and they will be shown in the following representation of *Celdeg* (Fig's. 8 – 14). In many cases, a single sample was analysed repeatedly after having been stored for various times in the refrigerator in order to verify that the storage had no effect on the results. The deviations found were smaller or of a similar order of magnitude as the standard uncertainty calculated for a single analysis. No background correction of the TOC data and in the HPAEC measurements was necessary, as was demonstrated by spot analyses of ACW-I and series D (data not shown). Owing to the consumption of protons associated with the degradation reactions of cellulose, pH was slightly decreasing with increasing reaction time according to the data shown later on (cf. section 3.2.2).

From the data given in Tables 2 – 6, *Celdeg* is calculated according to eqn's. (6) – (8). Plots of *Celdeg* as a function of reaction time are shown in Fig's. 8 – 14 for the various materials and experimental conditions tested. As can be expected, the degree of cellulose degraded based on the dry weight of solid remaining (*Celdeg*$_{DW}$) and the degree of cellulose degraded based on total dissolved carbon in solution (*Celdeg*$_{TOC}$) are identical within the range of experimental uncertainty. The degree of cellulose degraded based on total concentration of ISA (*Celdeg*$_{ISA}$) is an underestimate of the degree of cellulose degraded, because other degradation products than ISA can be expected to be formed. Therefore, *Celdeg*$_{ISA}$ will be smaller than *Celdeg*$_{DW}$ or *Celdeg*$_{TOC}$.

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[4] Representative HPAEC chromatograms of all types of samples are shown in the Appendix (Fig's. 27 – 34).

Tab. 2: *Overview of analytical results of degradation of Aldrich cellulose in the presence of Ca(OH)$_2$ at 90 °C and pH ~13.3. No dry weights of the residual cellulose fraction have been determined in these series. All solution concentrations are corrected for loss of water during keeping the samples in the oven as indicated by f_v.*

Time (d)	f_v	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	f_v	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	f_v	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)
		A90-1[a]				A90-2[b]				A90-3[c]		
0.25	1.002	4.35	5.58	942	1.002	4.74	6.14	1093	1.001	5.03	6.51	1197
0.97	1.006	7.11	9.34	1865	1.004	7.16	9.50	1889	1.004	7.31	9.48	1849
2	1.008	7.58	9.73	1899	1.009	7.35	9.64	1898	1.009	7.61	10.0	1961
7	1.012	7.71	10.2	1975	1.012	7.82	9.99	2031	1.010	7.79	10.3	2033
14	1.013	8.17	10.6	n.d.	1.013	7.86	10.5	n.d.	1.012	8.14	10.5	n.d.
22	1.015	7.76	9.32	2147	1.015	7.49	8.88	2062	1.014	8.42	9.92	2167
37	1.017	8.35	9.78	n.d.	1.018	7.69	9.16	n.d.	1.017	7.69	9.17	n.d.
57	1.021	8.29	9.75	2617	1.019	8.10	9.69	2720	1.019	8.56	10.1	2568
77	1.024	8.46	9.87	2394	1.023	8.53	10.1	2418	1.021	8.53	10.0	2642
102	1.027	7.72	9.13	2285	1.026	7.93	9.40	2803	1.025	6.63	7.99	2821
135	1.031	6.77	8.65	3097	1.030	6.52	8.55	3117	1.031	6.37	8.13	3059
193	1.035	4.88	7.61	n.d.	1.036	4.86	7.76	n.d.	1.036	5.23	7.97	n.d.
238	1.040	4.36	7.49	2938	1.041	4.17	7.90	3070	1.041	4.40	7.81	3099
322	1.049	2.94	5.85	3073	1.050	2.85	5.71	3090	1.051	3.08	6.03	3082
430	1.061	1.96	5.25	2970	1.060	1.57	4.12	2877	1.064	2.26	5.65	3255
539	1.076	0.91	3.35	2222	1.073	1.00	4.59	2961	1.078	1.23	4.67	2924
667	1.093	0.48	2.46	3012	1.090	0.74	3.46	2931	1.094	0.68	3.48	2746

[a] w_c^0: 10.1 g; V: 923 cm³   [b] w_c^0: 10.0 g; V: 925 cm³   [c] w_c^0: 10.0 g; V: 916 cm³

n.d. not determined

Tab. 3: *Overview of analytical results of degradation of Aldrich cellulose in the absence of Ca(OH)$_2$ at 90 °C and pH ~13.3 (series B90) and in the presence of Ca(OH)$_2$ at 90 °C and pH ~13.3 (series C90). All solution concentrations are corrected for loss of water during keeping the samples in the oven as indicated by f$_v$.*

| B90-1 [a] | | | | C90 [b] | | | | | | |
Time (d)	f_V	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	Time (d)	f_V	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	DP	w_C (g)
0.04	1.001	0.22	0.30	91							
1.00	1.001	4.11	7.52	2123	1	1.001	6.75	8.53	1809	114	1.409
2	1.003	4.11	7.78	2206							
7	1.005	4.72	8.70	2227							
15	1.007	4.45	8.13	n.d.	14	1.005	7.33	9.27	2192	101	1.258
23	1.009	4.75	8.62	2361							
35	1.015	5.03	8.97	n.d.							
50	1.018	5.08	9.11	n.d.							
70	1.020	4.98	8.41	2766	77	1.120	8.93	11.1	2952	64	1.032
95	1.023	4.91	8.41	n.d.							
128	1.026	4.93	8.59	3178	139	1.093	5.88	8.09	3225	52	0.942
184	1.031	4.71	8.36	3195							
231	1.037	4.71	7.89	3005							
315	1.045	4.23	7.99	3097	270	1.412	3.14	6.41	3276	49	0.908
423	1.056	3.49	7.05	3390	379	1.386	1.99	5.70	2931	44	0.882
532	1.069	3.63	5.71	3067							
661	1.085	4.09	8.56	2766							

[a] w_c^0: 10.0 g; *V*: 972 cm³   [b] The cellulose to liquid ratio differs from sample to sample

n.d. not determined

Tab. 4: *Overview of analytical results of degradation of cotton cellulose in the absence of Ca(OH)$_2$ at 90 °C and pH ~13.3 (series F90) and in the presence of Ca(OH)$_2$ at 90 °C and pH ~13.3 (series E90 and G90). All solution concentrations are corrected for loss of water during keeping the samples in the oven as indicated by f$_v$.*

E90

Time (d)	f$_V$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	DP	w$_C$ (g)
1	1.001	0.42	0.67	198	560	0.441
7	1.003	2.24	3.09	950	330	0.376
14	1.003	2.75	4.12	1352	280	0.341
37	1.044	4.03	5.72	2107	160	0.323
57	1.011	3.47	5.51	2001	93	0.255
77	1.017	3.59	5.39	2354	n.d.	n.d.
77	1.017	3.58	5.38	n.d.	68	0.262
105	1.030	2.98	5.32	2544	76	0.219
135	1.021	3.40	5.51	2532	96	0.221
191	1.036	2.48	4.67	2538	62	0.237
238	1.041	2.72	4.26	2708	n.d.	0.275
322	1.139	2.03	4.43	2662	115	0.227
378	1.078	0.86	3.49	2599	n.d.	0.210
487	1.124	0.67	3.39	2540	68	0.237
616	1.117	0.31	2.16	2048	70	0.232

F90

Time (d)	f$_V$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	DP	w$_C$ (g)
1	1.018	0.58	0.80	275	695	0.471
14	1.002	2.32	3.54	1178	257	0.410
77	1.034	2.17	3.87	1404	196	0.344
191	1.056	2.01	3.67	1513	163	0.302
322	1.049	1.76	3.02	1641	n.d.	0.300
491	1.211	2.02	4.28	1301	n.d	0.256
616	1.314	2.00	4.72	1366	n.d	0.252

G90

Time (d)	f$_V$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	DP	w$_C$ (g)
6	1	2.44	3.65	1432	1205	2.734
22	1.005	4.27	7.03	2732	1187	2.583
50	1.009	5.89	10.1	4161	907	2.434
99	1.023	5.18	10.9	6271	540	2.243
202	1.044	4.50	11.1	7106	n.d.	2.113
317	1.058	4.42	12.5	6159	n.d.	2.037

Tab. 5: *Overview of analytical results of degradation of Aldrich cellulose in the presence of Ca(OH)$_2$ at 90 °C and pH ~13.3. All solution concentrations are corrected for loss of water during keeping the samples in the oven as indicated by f$_v$.*

A90-4 (10 g·dm^{-3} cellulose, initially)					A90-5 (10 g·dm^{-3} cellulose, initially)				
Time (d)	f$_v$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm^{-3})	Time (d)	f$_v$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm^{-3})
60	1.038	7.19	9.20	3060	60	1.289	4.87	7.01	2735
60 [a]	1.038	1.50	1.85	649	60 [b]	1.289	0.21	0.31	124
61 [a]	1.040	1.49	1.88	613	61 [b]	1.290	0.20	0.29	85
63 [a]	1.041	1.48	1.85	507	63 [b]	1.292	0.20	0.36	111
67 [a]	1.042	1.32	1.79	669	67 [b]	1.294	0.18	0.36	126
74 [a]	1.044	1.16	1.59	622	74 [b]	1.296	0.13	0.24	91
83 [a]	1.045	1.00	1.46	623	83 [b]	1.298	0.10	0.24	149
90 [a]	1.046	0.93	1.60	656	90 [b]	1.301	0.085	0.22	136
111 [a]	1.051	0.54	1.29	701	111 [b]	1.304	0.044	0.095	108
139 [a]	1.055	0.20	1.00	691	139 [b]	1.309	0.021	0.065	131
217 [a]	1.064			482	217 [b]	1.319			109

A90-6 (2 g·dm^{-3} cellulose, throughout)					A90-7 (0.5 g·dm^{-3} cellulose, throughout)				
Time (d)	f$_v$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm^{-3})	Time (d)	f$_v$	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm^{-3})
1	1.010	1.33	1.52	355	1	1.009	0.39	0.43	101
3	1.013	1.49	1.78	368	3	1.012	0.41	0.45	99
7	1.015	1.62	2.04	486	7	1.015	0.37	0.68	122
14	1.018	1.48	1.88	493	14	1.020	0.31	0.41	121
30	1.021	1.12	1.69	608	30	1.024	0.19	0.33	141
51	1.030	0.71	1.43	657	51	1.030	0.16	0.37	139
79	1.037	0.33	1.16	681	79	1.038	0.10	0.32	157
157	1.050			706	157	1.063			157

[a] After diluting the reaction mixture by NaOH/KOH by a factor of 4.96.

[b] After diluting the reaction mixture by NaOH/KOH by a factor of 20.5.

Tab. 6: Overview of analytical results of degradation of Aldrich cellulose and cotton cellulose in the presence of $Ca(OH)_2$ at 60 °C and pH ~13.3 (series A60-2, C60 and E60). All solution concentrations are corrected for loss of water during keeping the samples in the oven as indicated by f_v.

A60-2 (10.06 g·dm⁻³)

Time (d)	f_v	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)
1	1.000	3.75	6.68	839
2	1.001	5.10	9.50	1136
5	1.002	4.14	8.01	1465
9	1.004	6.51	12.75	1635
16	1.005	7.08	14.43	1725
30	1.006	6.65	13.22	1870
54	1.007	7.88	10.53	2105
64	1.008	8.47	14.28	2192
86	1.009	8.47	14.46	2327
103	1.010	8.76	14.75	2404
118	1.011	8.59	11.51	2441
145	1.012	8.26	11.46	2502
182	1.013	8.62	9.83	2532
240	1.015	8.48	9.69	2520

C60

Time (d)	f_v	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	DP	w_c (g)
2	1.001	2.93	4.79	553	113	1.409
10	1.001	7.57	12.69	1574	121	1.179
20	1.002	7.41	14.37	1857	105	1.077
54	1.001	7.51	13.48	2433	78	0.912
64	1.004	7.84	14.34	2297	87	0.926
103	1.002	7.91	14.07	2574	60	0.800
145	1.002	8.33	14.67	2776	63	0.870
180	1.004	7.40	13.55	2541	55	0.835
308	1.014	7.77	9.21	2928	52	0.892
366	1.013	7.70	9.38	2933	50	0.781
366	1.009	7.32	8.83	2797	50	0.799

E60

Time (d)	f_v	[α-ISA] (mM)	[β-ISA] (mM)	TOC (mg·dm⁻³)	DP	w_c (g)
2	1.000	0.27	1.14	71	560	0.430
10	1.001	2.32	3.65	539	132	0.381
20	1.002	3.47	6.11	1020	199	0.319
54	1.002	4.26	6.60	1474	106	0.320
86	1.002	4.21	6.45	1559	98	0.275
118	1.007	4.11	7.80	1569	89	0.275
149	1.005	4.48	7.97	1649	86	0.258
180	1.010	4.58	7.67	1795	84	0.298
212	1.022	4.77	8.22	1880	90	0.325
244	1.010	4.05	7.73	1766	85	0.293
275	1.011	4.22	7.75	1831	79	0.277
308	1.030	3.52	4.82	1805	78	0.289
366	1.017	3.57	4.53	1767	74	0.283

Fig. 8:

Degradation of Aldrich cellulose in the presence of $Ca(OH)_2$ at pH 13.3 and T = 90°C (open symbols: A90, closed symbols: C90). The initial ratio of weight of cellulose to volume of liquid is ~10 $g \cdot dm^{-3}$. The data of series A90 are average values from three independent experiments. The error bars represent the maximum of the sample-to-sample variations and the experimental uncertainties calculated for the single measurements.
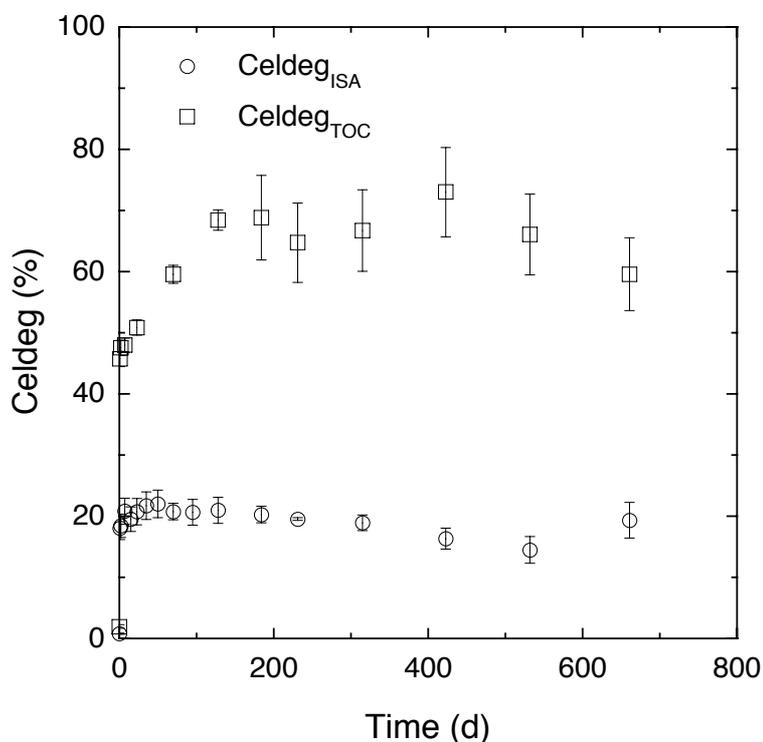
Fig. 9:

Degradation of Aldrich cellulose in the absence of $Ca(OH)_2$ at pH 13.3 and T = 90°C (series B90). The initial ratio of weight of cellulose to volume of liquid is ~10 $g \cdot dm^{-3}$. All data are from one single experiment. The error bars represent the experimental uncertainties calculated for the single measurements.
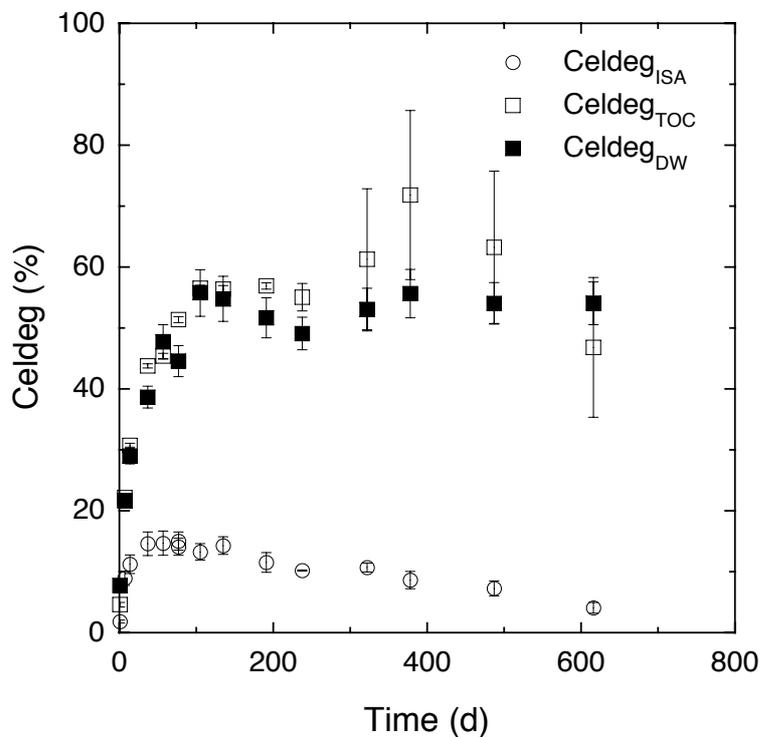
Fig. 10:

*Degradation of cotton cel-
lulose in the presence of
Ca(OH)₂ at pH 13.3 and
T = 90°C (series E90).
The initial ratio of weight
of cellulose to volume of
liquid is ~10 g·dm³. Each
time point represents the
results of one single inde-
pendent experiment. The
error bars represent the
experimental uncertainties
calculated for the single
measurements.*
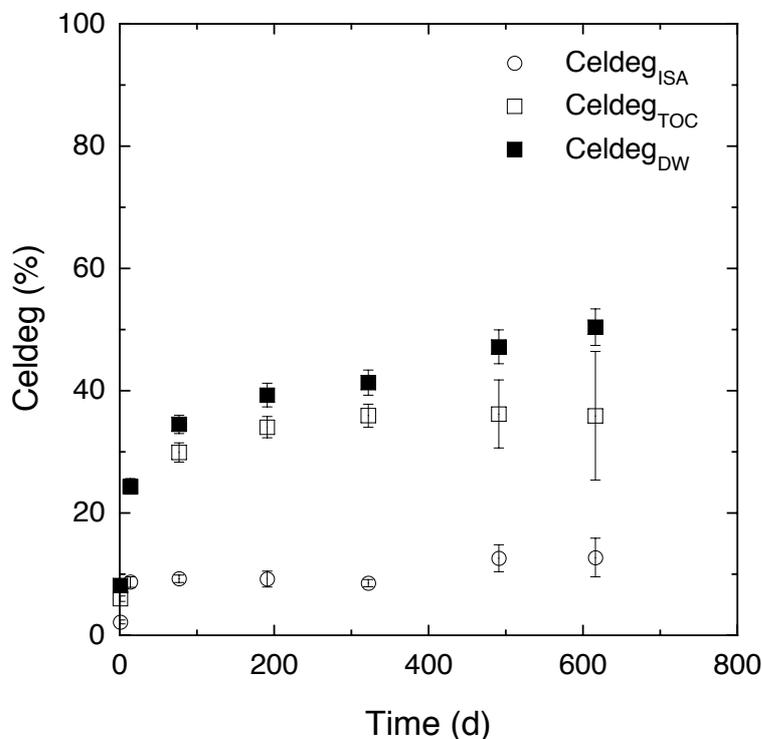
Fig. 11:

*Degradation of cotton cel-
lulose in the absence of
Ca(OH)₂ at pH 13.3 and
T = 90°C (series F90).
The initial ratio of weight
of cellulose to volume of
liquid is ~10 g·dm³. Each
time point represents the
results of one single inde-
pendent experiment. The
error bars represent the
experimental uncertainties
calculated for the single
measurements.*
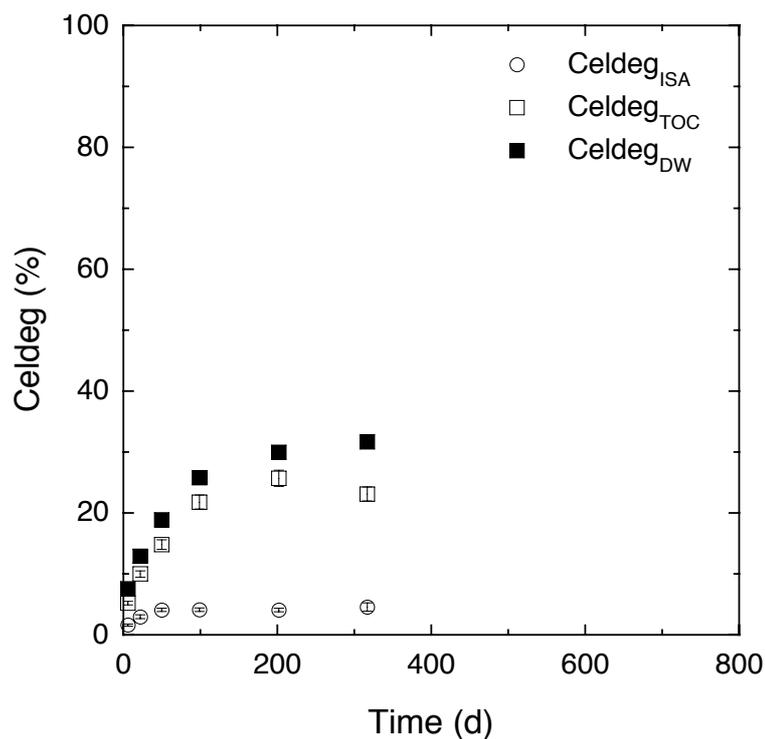
Fig. 12:

Degradation of cotton cellulose in the presence of $Ca(OH)_2$ at pH 13.3 and $T = 90°C$ (series G90). The initial ratio of weight of cellulose to volume of liquid is ~67 $g \cdot dm^{-3}$. Each time point represents the results of one single independent experiment. The error bars represent the experimental uncertainties calculated for the single measurements.
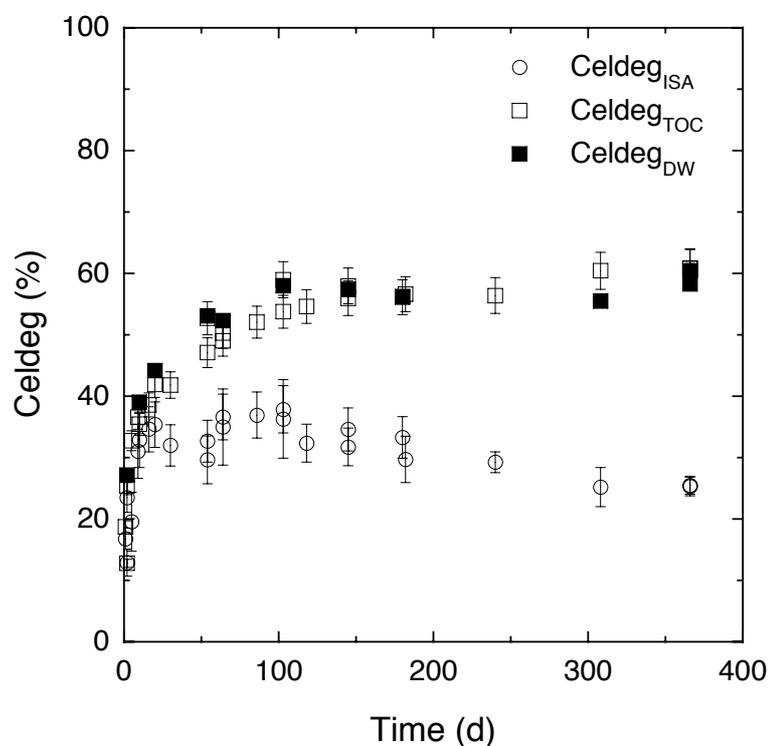
Fig. 13:

Degradation of Aldrich cellulose in the presence of $Ca(OH)_2$ at pH 13.3 and $T = 60°C$ (series A60-2 and C60). The initial ratio of weight of cellulose to volume of liquid is ~10 $g \cdot dm^{-3}$. The data of series A60-2 are from one single batch. The error bars represent the maximum of the sample-to-sample variations and the experimental uncertainties calculated for the single measurements.
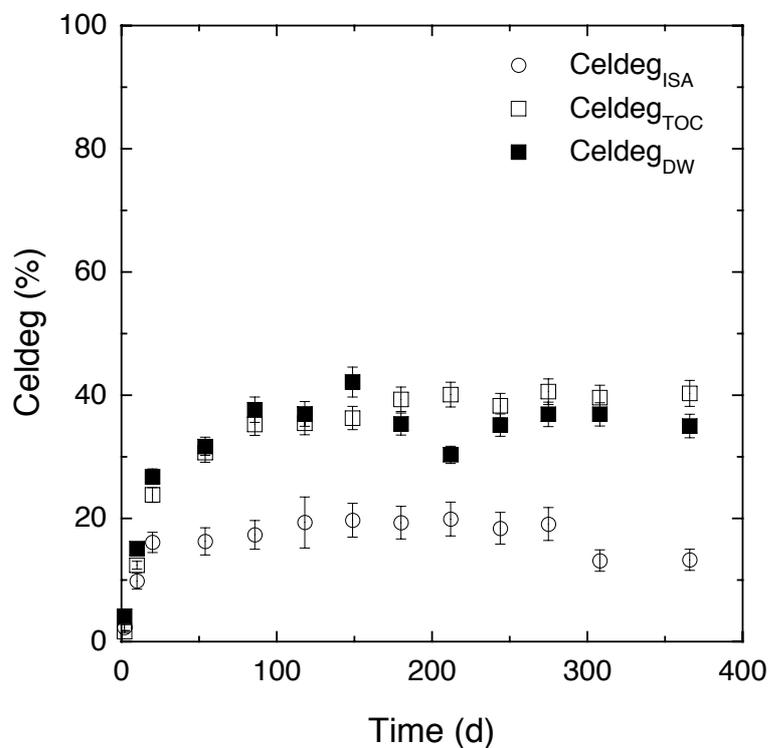
Fig. 14:

Degradation of cotton cellulose in the presence of $Ca(OH)_2$ at pH 13.3 and $T = 60°C$ (series E60). The initial ratio of weight of cellulose to volume of liquid was 10 $g \cdot dm^{-3}$. Each time point represents the results of one single independent experiment. The error bars represent the experimental uncertainties calculated for the single measurements.

3.2   Supporting information

3.2.1   Dilution of reaction suspensions

In the type of experiments carried out within the frame of this work, it is not easy to answer the question, whether or not the reaction has stopped after a certain contact time, or — alternatively — whether the reaction still continues at much slower reaction rates. This problem is further enhanced by the uncertainty inherently associated with the experimental measurements. Although the overall analytical uncertainties of single TOC measurements are estimated to be in general less than 2 – 3 %, the general impression from Fig's. 8 – 14 is that the overall uncertainty of the entirety of one dataset is of the order of 5 – 10 %. One idea to reduce these analytical problems would be to replace the solution phase by a fresh NaOH/KOH solution after completion of the peeling-off reaction phase. Any further slow continuation of cellulose degradation would easier be detected in such a solution devoid of dissolved carbon, than in the reaction mixtures usually containing of the order of 2 g·dm^{-3} of TOC. However, such experiments failed due to some unknown rapid continuation of the cellulose degradation, probably induced by the washing and drying steps of the solid products before resuspension in fresh NaOH/KOH. For this reason, this type of experiment has been abandoned and replaced by an experiment, in which the suspension was diluted with fresh NaOH/KOH solution after completion of the peeling-off reaction phase (A90-4 and A90-5). Such types of experiments indicate whether or not, the stopping of cellulose degradation, as suggested by the overall impression given by Fig's. 8 – 14, may be caused by the presence of the reaction products of cellulose degradation. As shown by the results given in Tab. 5, no continuation of cellulose degradation can be detected within a time span of ~200 days after completion of the peeling-off phase. A graphical representation of these data is given in Fig. 15. Note that the concentrations of ISA and TOC in the experiments A90-4 and A90-5 after the dilution step are in agreement with the calculated values within the range of experimental uncertainty (cf. Tab. 5). Further note that these values are obtained in independent cellulose degradation experiments carried out from the beginning at cellulose:solution ratios of 2 g·dm^{-3} and 0.5 g·dm^{-3} (A90-6 and A90-7), which are similar to the values obtained in series A90-4 and A90-5 after the dilution step. These control experiments thus show that the degree of cellulose degradation is independent of the cellulose:solution ratio. From these experiments it can be concluded that the reaction products do not have an influence on the reaction rate of cellulose degradation.
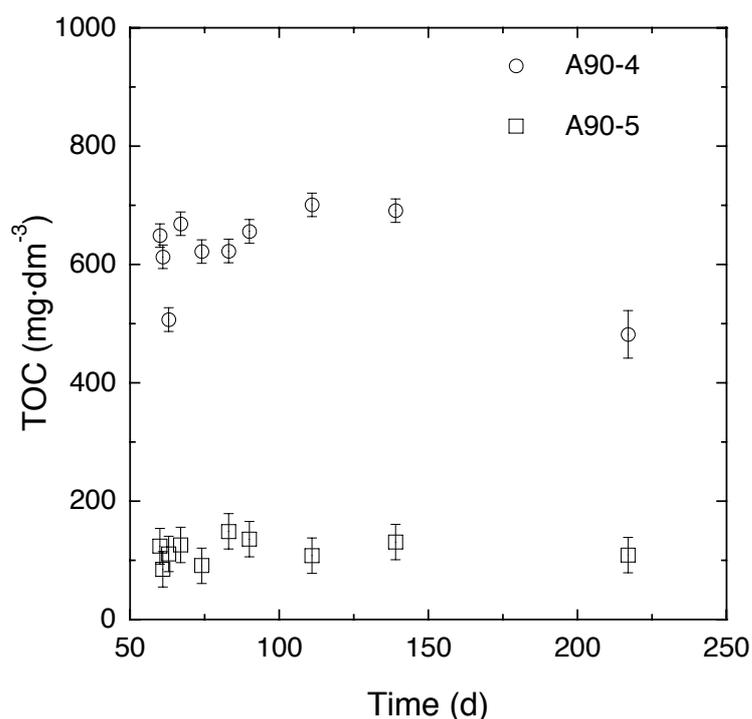
Fig. 15:

Degradation of Aldrich cellulose as monitored by TOC in the presence of $Ca(OH)_2$ at pH 13.3 and T = 90°C, after dilution of the suspensions by fresh NaOH/KOH mixture (A90-4 and A90-5). The initial TOC concentration before the dilution step was of the order of $3\,g\cdot dm^{-3}$ in both series (cf. Tab. 5).

3.2.2 Alkalinity titrations

Alkalinity titrations of the liquid phase of the cellulose degradation experiments have been carried out with the main purpose to check that the hydroxide concentration did not drop too much during the degradation of cellulose. As compared to simple pH measurements with a glass electrode, alkalinity titrations have the advantage that the experimental uncertainty of the hydroxide concentration calculated is much smaller, because potentiometric pH measurements in the region pH > 13 are inherently affected with systematic calibration and matrix effect problems. Furthermore, titration curves give information on the protonation constants of the carboxylic acids formed and on the possible presence of carbonate and bicarbonate in the systems. Fig. 16 shows the titration of sample C90-4 (Aldrich cellulose, reacted for 139 days), which is a typical titration curve for both Aldrich and cotton cellulose. As can be seen from this plot, the data between pH 12 and ~ 6 can be explained by the neutralisation of hydroxide ions. No carbonate can be detected, which would be expressed by a buffering region at pH

~10 and ~ 6.5[5]. In contrast, samples reacted for longer times than ~1 year showed measurable concentrations of carbonate in the titration curves. As will be shown later in the calculation of mass balances for carbon, carbonate is only a minor product of cellulose degradation. The pH region between 4 and 2 reveals the buffering action of carboxylic acids, as shown by the bump of the 1st derivative. Owing to the flatness of the titration curve no detailed analysis of protonation constants is possible, and the total concentration of these acids can only be roughly estimated. The estimated consumption of ~1.5 cm^3 HCl would correspond to a concentration of carboxylic acids of the order of 75 mM, which is clearly larger than the sum of concentrations of α-ISA and β-ISA (cf. Tab. 3). In agreement with the former observation that $Celdeg_{ISA}$ is much lower than $Celdeg_{TOC}$, this is a indication that the fragmentation (cf. Fig. 2) of monomeric cellulose units is an important pathway for cellulose degradation at elevated temperatures. The results of the titration of selected samples are summarised in Tab. 7. The results show that in those series, containing Aldrich cellulose and cotton cellulose at a cellulose to liquid ratio of 10 $g \cdot dm^{-3}$, the drop of pH during the experiments owing to the formation of carboxylic acids was within tolerable limits (less than 0.3 pH units). However, in series G90 (67 g cellulose per dm^3) this limit was slightly exceeded.

Fig. 17, which is representative for samples obtained from both the degradation of Aldrich cellulose and cotton cellulose at 60 °C, no significantly different features can be observed in titration curves from samples obtained from degradation experiments carried out at 90 °C and 60 °C.

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[5] A slight asymmetry of the 1st derivative can be anticipated, meaning that carbonate is present in trace amounts. Test experiments have shown that carbonate is detectable in such titrations at lowest amounts of the order of 5 μmol, corresponding to a detection limit for carbonate in the degradation solutions of ~2.5 mM.
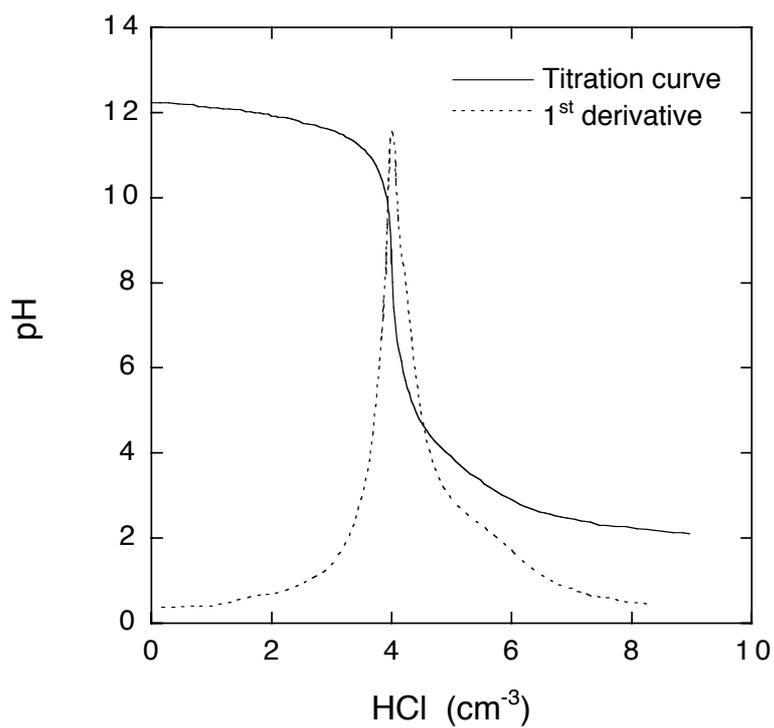
Fig. 16:

Titration of 2 cm³ of the supernatant of sample C90-4 (reacted for 139 d) with 0.1 M HCl in a volume of ~30 cm³.
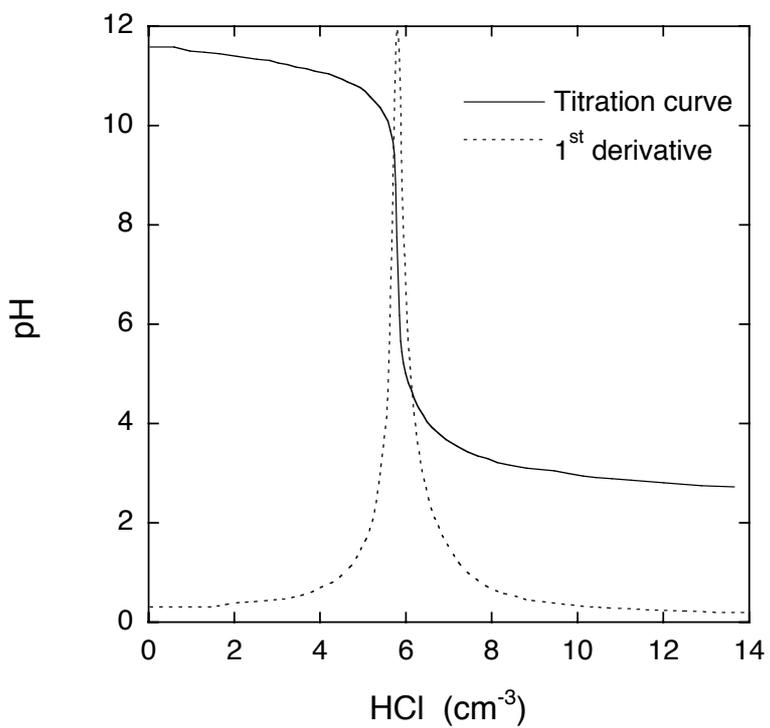
Fig. 17:

Titration of 0.5 cm³ of the supernatant of sample E60-6 (reacted for 366 d) with 0.02 M HCl in a volume of ~30 cm³.

Tab. 7: *Overview of the hydroxide concentrations calculated from alkalinity titrations of the liquid phases of selected samples from cellulose degradation solutions.*

	Experiments at 90 °C			Experiments at 60 °C	
Sample	$[OH^-]$ (M) [a]	pH [b]	Sample	$[OH^-]$ (M) [a]	pH [b]
A90-1, 6h	0.25	13.14	A60-2, 1d	0.27	13.17
A90-1, 77d	0.22	13.07	A60-2, 16d	0.26	13.14
A90-1, 430d	0.16	12.95	A60-2, 54d	0.24	13.11
A90-1, 667d	0.14	12.88	A60-2, 103d	0.24	13.11
B90-1, 184d	0.21	13.05	A60-2, 145d	0.24	13.11
B90-1, 424d	0.20	13.03	A60-2, 240d	0.23	13.09
C90-2, 14d	0.25	13.13	C60-11, 20d	0.25	13.13
C90-4, 139d	0.22	13.07	C60-1, 180d	0.24	13.12
C90-5, 270d	0.26	13.15	C60-3, 366d	0.19	13.01
C90-6, 430d	0.23	13.09	C60-4, 366d	0.20	13.03
D90-1, 14d	0.28	13.18	E60-16, 10d	0.27	13.17
D90-1, 212d	0.29	13.19	E60-3, 144d	0.23	13.09
D90-1, 322d	0.30	13.21	E60-11, 149d	0.25	13.12
E90-2, 7d	0.27	13.16	E60-1, 180d	0.24	13.11
E90-3, 14d	0.25	13.14	E60-5, 308d	0.23	13.10
E90-4, 21d	0.25	13.13	E60-6, 366d	0.23	13.10
E90-8, 105d	0.22	13.07	D60-1, 366d	0.29	13.20
E90-10, 191d	0.22	13.08			
E90-13, 378d	0.24	13.11			
E90-16, 616d	0.24	13.11			
F90-6, 491d	0.30	13.22			
F90-7, 616d	0.33	13.25			
G90-3, 49d	0.21	12.97			
G90-4, 99d	0.17	12.73			
G90-6, 317 d	0.067	12.56			

[a] Volume of HCl used up to the first pH jump of the titration curve at pH ~7. The results are not corrected for loss of water.

[b] Calculated using a logarithmic activity coefficient of –0.134 for protons and OH^-.

3.2.3   Elemental analyses

The results of elemental analyses are summarised in Tab. 8. These measurements serve the following purposes:

(i)   To check for possible changes in the calcium speciation owing to the formation of cellulose degradation products. Drastic changes in Ca concentration could have had unpredictable consequences for the cellulose degradation kinetics.

(ii)   To show possible glass corrosion during storage of the filtered samples in the refrigerator using the Si concentration as an indicator.

The results show that both of these processes are of secondary importance. Another idea behind these measurements was to follow the volume concentration owing to the evaporation of water during the time the experiments were left in the oven. However, the scatter in the data is obviously too large for such small changes to be perceived.

Tab. 8:   Overview of the results of elemental analyses of the liquid phases of selected samples from cellulose degradation solutions. All solution concentrations are corrected for loss of water during keeping the samples in the oven.

Sample	Ca (M)	Na (M)	K (M)	Si (M)
A-90-1, 7 d	$1.11 \cdot 10^{-3}$	$1.11 \cdot 10^{-1}$	$1.66 \cdot 10^{-1}$	$1.13 \cdot 10^{-4}$
A-90-1, 57 d	$1.21 \cdot 10^{-3}$	$1.13 \cdot 10^{-1}$	$1.69 \cdot 10^{-1}$	$5.62 \cdot 10^{-5}$
A-90-1, 238 d	$2.07 \cdot 10^{-4}$	$1.10 \cdot 10^{-1}$	$1.64 \cdot 10^{-1}$	$2.39 \cdot 10^{-3}$
A-90-1, 430 d	$3.60 \cdot 10^{-4}$	$1.20 \cdot 10^{-1}$	$1.77 \cdot 10^{-1}$	$2.71 \cdot 10^{-3}$
A-90-1, 667 d	$2.88 \cdot 10^{-4}$	$1.24 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$2.40 \cdot 10^{-3}$
B-90-1, 7 d	$5.85 \cdot 10^{-4}$	$1.13 \cdot 10^{-1}$	$1.68 \cdot 10^{-1}$	$7.13 \cdot 10^{-5}$
B-90-1, 70 d	$3.04 \cdot 10^{-4}$	$1.16 \cdot 10^{-1}$	$1.72 \cdot 10^{-1}$	$3.60 \cdot 10^{-3}$
B-90-1, 184 d	$3.45 \cdot 10^{-4}$	$1.23 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$4.02 \cdot 10^{-3}$
B-90-1, 231 d	$1.75 \cdot 10^{-4}$	$9.14 \cdot 10^{-2}$	$1.33 \cdot 10^{-1}$	$1.95 \cdot 10^{-3}$
B-90-1, 423 d	$2.46 \cdot 10^{-4}$	$1.05 \cdot 10^{-1}$	$1.48 \cdot 10^{-1}$	$2.20 \cdot 10^{-3}$
B-90-1, 661 d	$2.85 \cdot 10^{-4}$	$1.24 \cdot 10^{-1}$	$1.83 \cdot 10^{-1}$	$2.53 \cdot 10^{-3}$
C90-6, 378 d	$2.14 \cdot 10^{-4}$	$1.23 \cdot 10^{-1}$	$1.79 \cdot 10^{-1}$	$2.27 \cdot 10^{-3}$

Tab. 8 (continued)

E90-3, 14 d	$5.21 \cdot 10^{-4}$	$1.18 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$	$4.86 \cdot 10^{-3}$
E90-5, 57 d	$3.69 \cdot 10^{-4}$	$1.05 \cdot 10^{-1}$	$1.55 \cdot 10^{-1}$	$3.98 \cdot 10^{-3}$
E90-8, 105 d	$1.11 \cdot 10^{-4}$	$1.15 \cdot 10^{-1}$	$1.71 \cdot 10^{-1}$	$9.23 \cdot 10^{-4}$
E90-11, 238 d	$2.35 \cdot 10^{-4}$	$1.19 \cdot 10^{-1}$	$1.76 \cdot 10^{-1}$	$2.56 \cdot 10^{-3}$
E90-16, 616 d	$1.91 \cdot 10^{-4}$	$1.21 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$2.00 \cdot 10^{-3}$
F90-2, 14 d	$5.12 \cdot 10^{-4}$	$1.23 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$6.45 \cdot 10^{-3}$
F90-4, 191 d	$2.48 \cdot 10^{-4}$	$1.25 \cdot 10^{-1}$	$1.84 \cdot 10^{-1}$	$4.84 \cdot 10^{-3}$
F90-7, 616 d	$1.80 \cdot 10^{-4}$	$1.26 \cdot 10^{-1}$	$1.80 \cdot 10^{-1}$	$1.67 \cdot 10^{-3}$
G90-1, 6 d	$6.61 \cdot 10^{-4}$	$1.16 \cdot 10^{-1}$	$1.69 \cdot 10^{-1}$	$2.34 \cdot 10^{-4}$
G90-4, 99 d	$2.44 \cdot 10^{-4}$	$1.16 \cdot 10^{-1}$	$1.69 \cdot 10^{-1}$	$2.87 \cdot 10^{-3}$
ACW-I, 7 d	$5.63 \cdot 10^{-4}$	$1.15 \cdot 10^{-1}$	$1.74 \cdot 10^{-1}$	$6.72 \cdot 10^{-4}$
ACW-I, 57 d	$8.33 \cdot 10^{-4}$	$1.14 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$	$1.49 \cdot 10^{-4}$
D90-1, 14 d	$9.83 \cdot 10^{-5}$	$1.17 \cdot 10^{-1}$	$1.74 \cdot 10^{-1}$	$3.69 \cdot 10^{-4}$
D90-1, 77 d	$4.65 \cdot 10^{-4}$	$1.21 \cdot 10^{-1}$	$1.78 \cdot 10^{-1}$	$5.22 \cdot 10^{-3}$
D90-1, 184 d	$1.01 \cdot 10^{-4}$	$1.14 \cdot 10^{-1}$	$1.69 \cdot 10^{-1}$	$1.27 \cdot 10^{-3}$
D90-1, 320 d	$4.79 \cdot 10^{-4}$	$1.16 \cdot 10^{-1}$	$1.74 \cdot 10^{-1}$	$6.87 \cdot 10^{-4}$
A60-2, 2 d	$1.37 \cdot 10^{-3}$	$1.22 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$2.79 \cdot 10^{-4}$
A60-2, 30 d	$1.67 \cdot 10^{-3}$	$1.21 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$2.47 \cdot 10^{-4}$
A60-2, 103 d	$1.71 \cdot 10^{-3}$	$1.20 \cdot 10^{-1}$	$1.80 \cdot 10^{-1}$	$1.37 \cdot 10^{-4}$
A60-2, 145 d	$1.66 \cdot 10^{-3}$	$1.21 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$1.95 \cdot 10^{-4}$
C60-9, 2 d	$1.42 \cdot 10^{-3}$	$1.17 \cdot 10^{-1}$	$1.78 \cdot 10^{-1}$	$2.79 \cdot 10^{-4}$
C60-11, 20 d	$1.62 \cdot 10^{-3}$	$1.18 \cdot 10^{-1}$	$1.80 \cdot 10^{-1}$	$5.40 \cdot 10^{-5}$
C60-6, 64 d	$1.78 \cdot 10^{-3}$	$1.23 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$1.70 \cdot 10^{-4}$
C60-1, 180 d	$7.03 \cdot 10^{-4}$	$1.06 \cdot 10^{-1}$	$1.58 \cdot 10^{-1}$	$4.03 \cdot 10^{-4}$
E60-18, 2 d	$1.13 \cdot 10^{-3}$	$1.16 \cdot 10^{-1}$	$1.76 \cdot 10^{-1}$	$9.10 \cdot 10^{-5}$
E60-17, 20 d	$1.38 \cdot 10^{-3}$	$1.16 \cdot 10^{-1}$	$1.76 \cdot 10^{-1}$	$2.70 \cdot 10^{-4}$
E60-9, 86 d	$1.18 \cdot 10^{-3}$	$1.21 \cdot 10^{-1}$	$1.80 \cdot 10^{-1}$	$2.96 \cdot 10^{-4}$
E60-4, 275 d	$4.18 \cdot 10^{-4}$	$1.20 \cdot 10^{-1}$	$1.79 \cdot 10^{-1}$	$1.55 \cdot 10^{-3}$
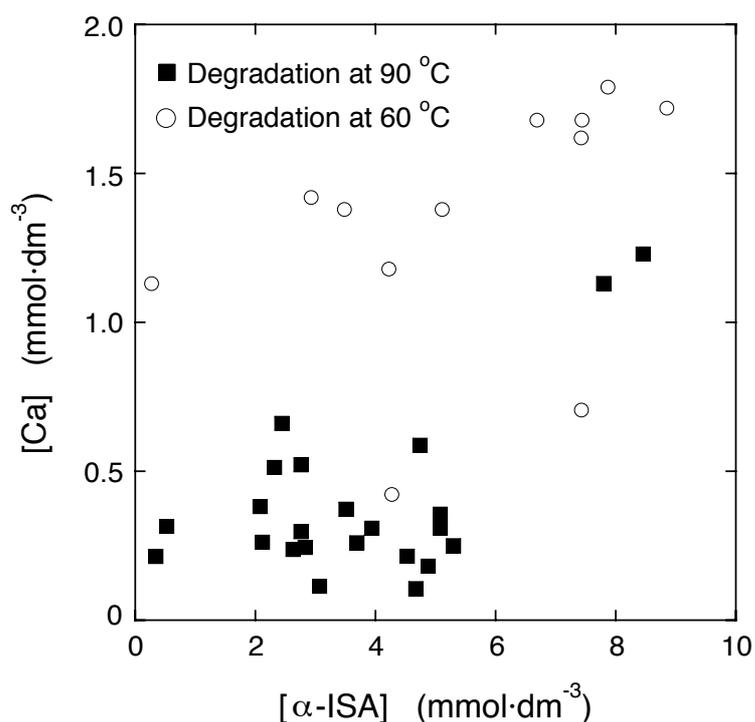
Fig. 18:
Dependence of total concentration of Ca on the concentration of α-ISA in cellulose degradation solutions obtained from 60 °C and 90 °C experiments.

The ICP-OES data show an interesting correlation between total Ca concentration and the concentration of α-ISA. It is shown by Fig. 18 that the Ca concentration is increasing with the concentration of α-ISA. This can be understood with respect to the fact that α-ISA is forming stable complexes with Ca^{2+} at alkaline pH (VAN LOON & GLAUS, 1998; VERCAMMEN, 2000; VERCAMMEN et al., 1999). The fact that two separate correlation function exist for the degradation systems at 60 °C and 90 °C can be explained due to different solubilities of $Ca(OH)_2$ at these temperatures. The solubility of $Ca(OH)_2$ increases with decreasing temperature. Fig. 18 suggests that α-ISA may be the dominant ligand with respect to complexation of hard cations. This is an interesting information with respect to the question of the possible formation of strong ligands as minor products of the degradation of cellulose.

3.2.4   Other degradation products than ISA and mass balance for carbon

A series of samples has been analysed using HPIEC for the presence of acetate, formiate, glycolate and lactate, which have been previously identified as important short-chain carboxylic acids being produced during the degradation of cellulose (GLAUS et al., 1999). The results are presented in Tab. 9. Representative HPIEC chromatograms of all types of samples are shown in the Appendix (Fig's. 35 – 39).

Tab. 9: Overview of the results of HPIEC analyses in supernatants of cellulose degradation. All solution concentrations are corrected for loss of water during keeping the samples in the oven.

Sample	[Glycolate] (mM)	[Formiate] (mM)	[Lactate] (mM)	[Acetate] (mM)
A90-1, 37d	1.79	10.3	2.68	1.42
A90-1, 57d	2.42	8.42	2.99	1.67
A90-1, 77d	3.41	10.5	3.65	2.59
A90-1, 102d	3.82	10.0	3.65	2.95
A90-1, 135d	6.51	14.0	5.08	5.47
A90-1, 193d	8.16	14.3	5.23	7.12
A90-1, 322d	11.8	16.6	6.38	10.2
A90-1, 539d	11.9	14.7	5.51	10.7
A90-1, 667d	16.9	19.7	7.97	15.6
B90-1, 35d	1.60	15.7	2.92	1.30
B90-1, 315d	7.55	24.6	7.50	5.51
B90-1, 532d	7.43	22.5	7.10	5.51
B90-1, 661d	6.57	27.3	8.87	7.17
E90-4, 37d	4.58	9.16	2.42	2.59
E90-5, 57d	5.01	9.21	2.38	3.48
E90-6, 77d	7.21	11.8	3.42	5.24
E90-8, 105d	7.83	12.0	3.57	6.05
E90-9, 135d	6.56	11.3	3.41	4.76
E90-10, 191d	9.39	14.5	4.45	7.30
E90-11, 238d	7.52	11.3	3.67	5.48
E90-12, 322d	10.5	15.2	4.94	8.42
E90-13, 378d	10.0	12.3	4.12	8.32
E90-14, 487d	10.9	13.0	4.57	8.99
E90-16, 616d	13.0	14.6	5.3	10.3

Tab. 9 (continued)

A60-2, 16d	0.55	4.02	1.29	0.58
A60-2, 145d	2.28	7.48	2.75	1.80
A60-2, 182d	2.58	7.70	2.91	2.05
E60-8, 54d	2.52	5.61	1.08	1.55
E60-3, 244d	4.31	8.41	2.24	3.27
E60-5, 308d	4.44	8.00	2.03	3.34

From a combination of these data with the ISA data from the HPAEC measurements (Tables 2, 4 and 6) mass balances for carbon concentrations are calculated for the A- and E series degraded at 60 °C and 90 °C. The mass balances are completed by two other types of carbon: (i) the sum of unidentified carboxylic acids (abbreviated as UICA in the following) detected in the HPIEC measurements[6] and (ii) carbonate as detected in the alkalinity titrations. The assumption that C_4-, C_5- or C_6- mono- or dicarboxylic acids may be formed during the degradation is justified, because such compounds have been described in the literature to be formed under similar degradation conditions (ALFREDSSON & SAMUELSON, 1968; LÖWENDAHL et al., 1976; PETERSSON & SAMUELSON, 1976). The response factors[7] and the number of carbon atoms of the UICA are not exactly known. The sum of their concentrations can, nevertheless, be calculated rather reliably, because the response factors are mainly depending on the retention times of the analytes and are rather independent of their charge. An average response factor based on a large series of known carboxylic acids eluting between 5 and 20 min. can therefore be used for this calculation. Further it has been assumed that the unidentified carboxylic acids contain 4 ±2 carbon atoms on the average. This uncertainty covers most of the acids known as cellulose degradation products. Similar uncertainties are also encountered in the case of carbonate. The endpoint of the buffering action of the carbonate-bicarbonate couple can only tentatively estimated from the titration curve, because carbonate is present only in minor amounts in the degradation solutions. Further the buffering region of the bicarbonate-carbon dioxide couple is blurred by the dominant buffering action of the various carboxylic acids

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[6] For an overview of these peaks, the reader is referred to the chromatograms shown in the Appendix (cf. Fig's. 35 – 39).

[7] Relating peak height and peak area to the amount of analyte injected.

present in the degradation solutions. For these reasons, the carbonate concentrations are affected by relatively large uncertainties. However, the endpoints for carbonate have been chosen such that the resulting carbonate concentrations are rather overestimated than underestimated. Despite all these uncertainties, the assumption of a relative uncertainty of 50 % for the sum of concentrations of unidentified carboxylic acids and for carbonate concentrations is rather on the safe side. A summary of the different fractions of carbon, their sum and a comparison based on carbon concentration with the total concentration of carbon as determined by TOC measurements is shown in Tables 10 and 11. As can be taken from these tables, the measured TOC values can largely be explained by the compounds specified in Tab's 10 and 11. In most cases, the mass balances do not account for the full amount of TOC measured even when considering the uncertainties involved in these calculations. Note that the fractions of identified carbon species for cellulose degradation carried out at 60 °C are similar to those values measured at room temperature (GLAUS et al., 1999), where values between 80 and 90 % were found. For cellulose degradation carried out at 90 °C these values seem to be somewhat lower, especially in the case of cotton cellulose.

An interesting and unexpected feature of the experiments carried out at 90 °C (cf. Fig's. 8 and 10), is the decrease of the concentration of ISA with increasing reaction time during the stationary reaction phase, during which almost no cellulose is degraded. Indications for such a process in the literature can only be found in ALFREDSSON et al. (1961), where the disappearance of ISA at 170 °C in ~2 M NaOH has been observed to occur within ~20 days. However, no reaction products have been characterised in that work. A closer inspection of Tables 2 and 4 reveals that the decrease observed in this work is mainly caused by a decrease in the concentration of α-ISA. This process can probably be explained by an unknown type of fragmentation of α-ISA. It can be hypothesised that the fragmentation of α-ISA is induced by the sorption of α-ISA to the surface of $Ca(OH)_2$, because it is much less evident in the degradation series in which no $Ca(OH)_2$ is present (cf. Fig's. 9 and 11). A recent review article of ANGYAL (2001) shows that, despite almost one century of research, "new" reaction mechanisms are still discovered in the chemistry of carbohydrates at alkaline conditions. Such mechanisms often comprise rearrangement reactions induced by formation of complexes with metal cations. Note that an epimerisation from α-ISA to β-ISA (analogous e.g. to the epimerisation of β-MSA, see ALFREDSSON & SAMUELSON (1962)) can be excluded, because no stoichiometric increase of the concentration of β-ISA is observed. Further note that chemical transformations of α-ISA could not have

Tab. 10: Mass balance for carbon in the cellulose degradation experiments carried out at 90 °C. The reference to the TOC values is taken from Tables 2 and 4.

Time (d)	α-ISA + β-ISA Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	ICA[a] Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	UICA[b] Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	[CO₃²⁻] Carbon[d] (mg·dm⁻³)	c.a.u[e,g] (mg·dm⁻³)	% of TOC	Sum[c] Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	c.r.u[f] (%)
Series A90-1																
37	1305	167	56	297	30	13	263	131	11	*20*	*10*	1	1885	215	80	11
57	1299	167	50	307	31	12	629	314	24	*40*	*20*	2	2275	358	87	16
77	1320	123	55	401	40	17	595	298	25	*60*	*30*	3	2376	326	99	14
102	1213	113	53	414	41	18	638	319	28	*80*	*40*	4	2346	344	103	15
135	1110	105	36	638	64	21	1128	564	36	*100*	*50*	3	2977	579	96	19
193	899	55	30	727	73	24	782	391	26	*120*	*60*	4	2528	406	84	16
322	633	43	21	957	96	31	691	346	22	180	90	6	2461	372	80	15
539	307	49	14	916	92	41	610	305	27	*250*	*125*	11	2082	345	94	17
667	212	45	7	1303	130	43	778	389	26	348	174	12	2640	448	88	17
Series E90																
37	702	93	33	369	37	18	369	185	18	*17*	*9*	1	1457	210	69	14
57	647	88	32	400	40	20	787	394	39	*18*	*9*	1	1852	405	93	22
77	647	64	27	564	56	24	984	492	42	*19*	*10*	1	2213	499	94	23
105	598	61	23	606	61	24	874	437	34	*40*	*20*	2	2117	446	83	21
135	642	64	25	530	53	21	778	389	31	60	30	2	1949	398	77	20
191	515	72	20	735	73	29	907	454	36	*80*	*40*	3	2237	467	88	21
238	503	4	19	580	58	21	758	379	28	*100*	*50*	4	1941	387	72	20
322	465	33	17	815	81	31	1066	533	40	*120*	*60*	5	2466	543	93	22
378	313	51	12	736	74	28	706	353	27	121	61	5	1876	369	72	20
487	292	49	12	797	80	31	821	410	32	192	96	8	2102	432	83	21
616	178	39	9	927	93	45	393	197	19	211	106	10	1709	245	83	14

[a] Identified carboxylic acids: glycolate, formiate, lactate, acetate
[b] Unidentified carboxylic acids
[c] Sum: α-ISA + β-ISA + ICA + UICA + CO3
[d] Sum of carbon concentrations
[e] Combined absolute uncertainty
[f] Combined relative uncertainty
[g] Estimated values (by interpolation) in Italics

Tab. 11: Mass balance for carbon in the cellulose degradation experiments carried out at 60 °C. The reference to the TOC values is taken from Tab. 6.

Time (d)	α-ISA + β-ISA Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	ICA[a] Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	UICA[b] Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	$[CO_3^{2-}]$ Carbon[d] (mg·dm⁻³)	c.a.u[e,g] (mg·dm⁻³)	% of TOC	Sum[c] Carbon[d] (mg·dm⁻³)	c.a.u[e] (mg·dm⁻³)	% of TOC	c.r.u[f] (%)
Series A60-2																
16	1549	164	90	122	12	7	162	81	9	0	10	0	1832	184	106	10
145	1503	137	60	287	29	11	410	205	16	0	10	0	2200	249	88	11
192	1328	169	52	308	31	12	403	201	16	0	10	0	2039	265	81	13
Series E60																
54	782	106	53	204	20	14	280	140	19	0	10	0	1266	177	86	14
244	848	120	48	363	36	21	330	165	19	0	10	0	1542	207	87	13
308	600	79	33	356	36	20	624	312	35	0	10	0	1580	324	88	21

[a] Identified carboxylic acids: glycolate, formiate, lactate, acetate
[b] Unidentified carboxylic acids
[c] Sum: α-ISA + β-ISA + ICA + UICA + CO3
[d] Sum of carbon concentrations
[e] Combined absolute uncertainty
[f] Combined relative uncertainty
[g] Estimated values (by interpolation) in Italics

been observed in the previous studies on cellulose degradation (VAN LOON & GLAUS, 1998), because the stability of α-ISA in ACW-I has only been investigated in homogeneous solutions lacking of any solid phases.

In order to corroborate the hypothesis of fragmentation of α-ISA, the increase of concentration of carboxylic acids analysed in HPIEC has been compared to the decrease of total concentration of ISA during the reaction phase, in which TOC remains constant. The results are shown in Tab. 12 for the degradation of Aldrich cellulose and cotton cellulose at 90 °C. As can be seen from Tab. 12, the loss of α-ISA can well be explained by the increase in concentration of short-chain carboxylic acids, which suggests that ISA is not stable on a long term under the condition of the experiments. It would certainly be of interest to further investigate this process, in order to be able to assess its significance in the calculation of pore water concentrations of ISA under repository conditions.

Tab. 12: *Mass balance for the decrease of α-ISA concentration as compared to the increase of short-chain aliphatic acid during the constant reaction phase of cellulose degradation at 90 °C.*

	[Glycolate] (mM)	[Formiate] (mM)	[Lactate] (mM)	[Acetate] (mM)	[α-ISA] (mM)	Yield (%)[a]
A90-1, 322d	11.8	16.6	6.38	10.2	8.80	
A90-1, 667d	16.9	19.7	7.97	15.6	2.94	
Difference	5.13	3.08	1.58	5.36	-5.85	82
E90-4, 37d	4.58	9.16	2.42	2.59	9.75	
E90-16, 667d	13.0	14.6	5.34	10.3	2.47	
Difference	8.46	5.40	2.92	7.72	-7.28	106

[a] Calculated on the base of carbon concentration (1 C for formiate, 2 C for glycolate and acetate, 3 C for lactate and 6 C for α-ISA): Increase of the sum of carboxylic acids concentration expressed as percentage of the decrease of concentration of α-ISA.

4   DISCUSSION

4.1   Qualitative model comparison

For the following discussion, all the experimental data from the main experiments — with exception of series G90 — are considered. In series G90, the pH has dropped too much, which leads to a noticeable slowdown of the degradation reaction, i.e. the reaction rate constants are subject to changes with increasing reaction time, which is in principle also the case for the other experimental systems, however to a much lesser extent. The influence of the presence of $Ca(OH)_2$ on the degradation reaction is negligible in the case of Aldrich cellulose. Consequently all data from series A90, B90 and C90 can be taken together into a single dataset. The same has been done for the data of A60-2 and series C60. For the degradation series E90 and F90, the situation is less clear. The reaction in series F90 seems to proceed, by some unknown reasons, slightly slower than in series E90. Note that the cellulose to liquid ratio is identical in both series. It has further to be noted that samples F90-6 (492 d) and F90-7 (616 d) are affected by increased uncertainties owing to the unusually large loss of water during incubation of the samples in the oven (cf. Tab. 4). For this reason, the results of series F90 have to be interpreted with caution. However, for the conclusions drawn in the following, the discrepancy is of secondary importance. As shown by the results of series A90-1, A90-2 and A90-3, the sample-to-sample variability is of similar order of magnitude as the analytical uncertainties for the measurement of a single sample.

In view of the differences in DP (~120 for Aldrich cellulose and ~1700 for cotton cellulose) and in view of the scenarios proposed in the Introduction (cf. section 1.4), the evolution of *Celdeg* as a function of reaction time has shown an unexpected behaviour in two respects (cf. Fig's. 8 – 14). First, there is almost no substantial difference in cellulose degradation when comparing the results obtained at 60 °C and 90 °C. Second, there is almost no substantial difference in cellulose degradation when comparing the results obtained for Aldrich cellulose and cotton cellulose. Note that in cellulose degradation experiments carried out at comparable conditions at 25 °C, clear differences with respect to the degree of cellulose degradation were observed between those two cellulose materials (VAN LOON & GLAUS, 1998). However, in those experiments the time window of ~3 years was restricted to the observation of peeling-off processes only.

From the various scenarios shown in Fig. 6, scenario #1 can be ruled out with respect to the results obtained both for Aldrich cellulose and cotton cellulose. This scenario predicts the complete degradation of cellulose within a few hours for a temperature of 90 °C. The present experiments show that after a reaction time of 1 year, the degradation of cellulose is only incomplete. Similar conclusions can also be drawn for scenario #3. This scenario predicts that, after a rapid initial phase of peeling-off reaction, only minor changes in *Celdeg* occur owing to the alkaline hydrolysis. Within one year, the increase of *Celdeg* due to alkaline hydrolysis[8] is predicted to be of the order of < 5 %, which is clearly less than observed in the experiments. An attempt to explain the observed behaviour would be to use the temperature extrapolation of the reaction rate constant for the alkaline hydrolysis reaction (k) according to scenario #2, which is represented by the simulations shown in Fig. 19 for Aldrich cellulose and for cotton cellulose. As a consequence of this scenario, one has to conclude that the reaction rate is noticeably larger than predicted by the linear regression of the high temperature data of LAI & SARKANEN (1967). However, the consequence of such a
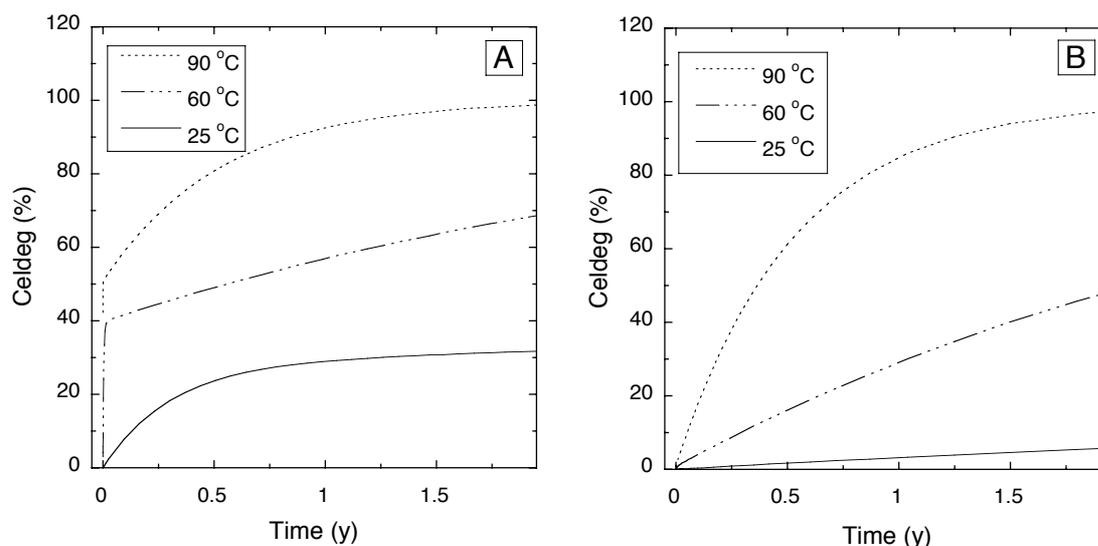
Fig. 19:
Predictions for the dependence of Celdeg as a function of time for Aldrich cellulose (plot A) and for cotton cellulose (Plot B). The reaction rate constants were calculated for the different temperatures using scenario #2 (cf. Fig. 6).

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[8] The degradation of cellulose is initially dominated by the peeling-off reaction, which proceeds much faster than the alkaline hydrolysis. The fraction of cellulose degraded during this initial phase is consequently not comprised in the term "*Celdeg* due to alkaline hydrolysis".

large reaction rate constant k would be the complete degradation of the cellulose material. The stopping of the degradation reaction, as observed for both Aldrich and cotton cellulose during the phase of alkaline hydrolysis, cannot be explained. Consequently the combined model of peeling-off reaction and alkaline hydrolysis of cellulose cannot explain satisfactorily the experimental results presented in this report. The model would have to be extended by a stopping of the alkaline hydrolysis, probably taking place at the crystalline phases of cellulose. However, no analytical expression is available from literature work to include such a type of reaction, although incomplete degradation of cellulose has been frequently observed at temperatures even larger than 170 °C (GARVES, 1985; NIEMELÄ, 1987, 1988; NIEMELÄ & SJÖSTRÖM, 1986). Summarising, the results can be described by a triple-phase reaction sequence:

(i)   The peeling-off of monomeric units of cellulose. This reaction phase is pronounced in the case of Aldrich cellulose, whereas almost negligible in the case of cotton.

(ii) A further continuation of cellulose degradation at a slower reaction rate. Whether this reaction is a continuation of the peeling-off process due to an increase in accessibility of "hidden" reducing end groups or caused by alkaline mid-chain scission cannot be decided based on such a qualitative consideration.

(iii) A complete stopping of the degradation reaction, resulting in an incomplete degradation of cellulose.[9]

Note that — when looking only at the *Celdeg* results — the data obtained for cotton cellulose could alternatively be explained by a reaction sequence completely dominated by the peeling-off process, which in turn could then be an explanation for the complete stopping of the degradation reaction. However such an assumption is in stark contrast to the observed results for DP_t, the *DP* expressed as a function of reaction time. A consequence of the formal understanding of the peeling-off process is that DP_t is linearly proportional to the fraction of unreacted cellulose, which is expressed by the experimental data in the following equation (DP_0 is the initial *DP*):

$$DP_t = \left(1 - \frac{Celdeg}{100}\right) \cdot DP_0 \tag{9}$$

A graphical comparison between DP_t, modeled for a pure peeling-off reaction and the experimental data obtained in series E-90 is shown in Fig. 20. Both *Celdeg*$_{TOC}$ and

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[9] Because no mechanistic understanding exists for the type of stopping observed in the present work, no attempt is made in this report to use this feature in a cellulose degradation model.

Celdeg$_{DW}$ (taken from Tab. 4) were used to calculate DP_t. The plot shows that the experimental data are not in agreement with the assumption of a pure peeling-off process. Less clear is the situation for Aldrich cellulose, as is demonstrated in Fig. 21. During the very fast initial reaction phase, by which ~ 40 % of cellulose is degraded, the DP_t of cellulose is virtually unchanged (cf. Tab. 3). The measured DP_0 of Aldrich cellulose is of the order of 120. It can be hypothesised that the statistic model for the peeling-off process reaches its limits of validity with "small" molecules, such as Aldrich cellulose. For this reason, the comparison between experimental DP_t and DP_t calculated for a pure peeling-off process is less fruitful in the case of Aldrich cellulose.
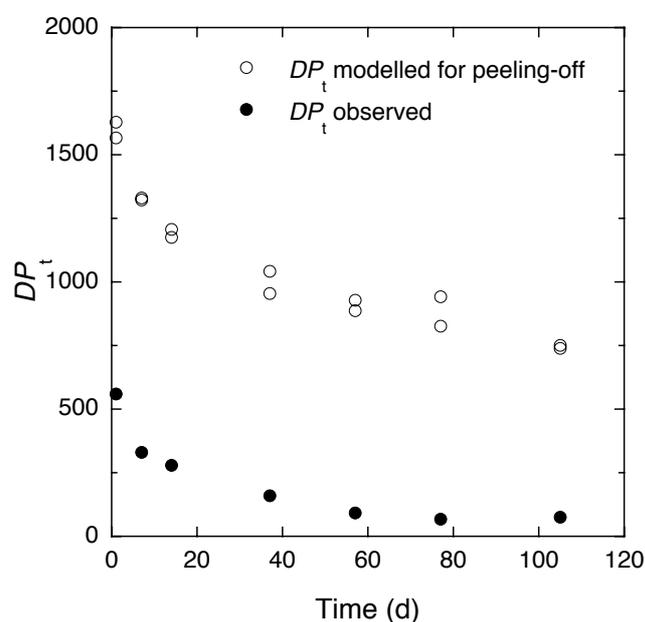
Fig. 20:
Plot of the dependence of DP on reaction time for series E90. The experimental data are compared with a model that is based on the peeling-off process solely. The model assumes a decrease in DP proportional to the fraction of unreacted cellulose and an initial DP of 1700 for cotton cellulose (experimental value).
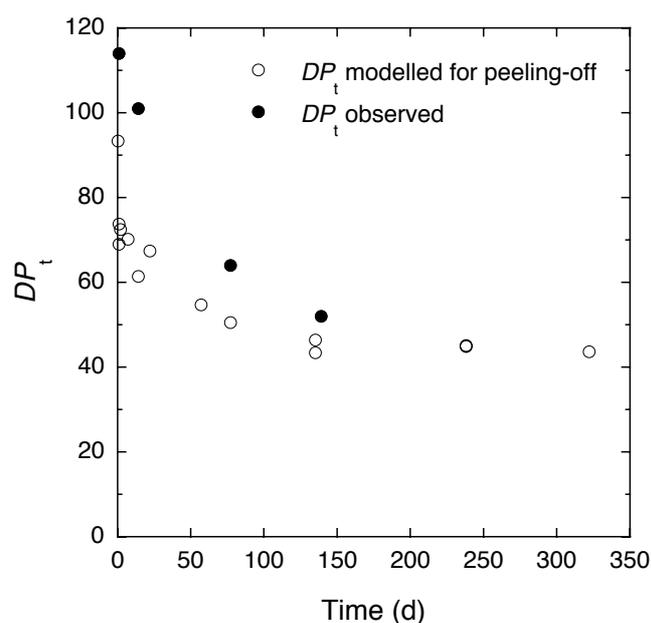
Fig. 21:
Plot of the dependence of DP on reaction time for series A90. The experimental data are compared with a model, that is based on the peeling-off process solely. The model assumes a decrease in DP proportional to the fraction of unreacted cellulose and an initial DP of 120 for Aldrich cellulose (experimental value).

4.2   Attempt to quantitatively model the alkaline hydrolysis

4.2.1   Evaluation based on *Celdeg*

With respect to the considerations made in section 4.1, the alkaline hydrolysis can —
at best — only be observed within a narrow phase of reaction. For the evaluation of *k*,
it is necessary to define this reaction phase (in the following referred to as the "second
reaction phase", according to the classification given in section 4.1), which may be
dominated by the alkaline hydrolysis. This is, to a certain degree, a subjective decision.
As a working hypothesis, this reaction phase is defined as $1\,d < t < 135\,d$ in the case of
Aldrich cellulose at 90 °C, as $7\,d < t < 105\,d$ for cotton cellulose at 90 °C, as $5\,d < t <$
$145\,d$ in the case of Aldrich cellulose at 60 °C, as $20\,d < t < 149\,d$ for cotton cellulose
at 90 °C. According to LAI & SARKANEN (1967), the kinetics of the alkaline hydrolysis
reaction are described by the following equation:

$$\ln\,(Y) = -\,k \cdot t = -\,k' \cdot \overline{x}_n \cdot t \tag{10}$$

Y is the fraction of unreacted cellulose and $\overline{x}_n$ the number of monomeric units peeled-
off on the average upon the mid-chain scission of a cellulose chain induced by the
alkaline hydrolysis. A graphical representation of the experimental data within the
ranges specified above adopted to eqn. (10) is given in Fig's. 22 and 23 for the
reaction at 90 °C and in Fig's. 24 and 25 for the reaction at 60 °C[10]. For these
evaluations, *Celdeg*$_{TOC}$ and *Celdeg*$_{DW}$ data were pooled.

Because this evaluation is only a test for a possible degradation of cellulose by alkaline
hydrolysis, different labels for the reaction rates involved are used in analogy to
eqn. (10):

$$\ln\,(Y) = -k_{obs} \cdot t = -k'_{obs} \cdot \overline{x}_n \cdot t \tag{11}$$

---

[10] Note that the data in these plots have undergone a "blank" correction for the peeling-off
process, i.e. time and *Celdeg* values have been linearly corrected, in order to cancel the
peeling-of phase, which is again a subjective decision. This correction does not affect the
slope of the regression line, which is used to calculate the reaction rate constant for alkaline
hydrolysis.

k_{obs} and k'_{obs} have to be regarded as adjustable reaction coefficients, rather than as reaction rate constants. They are evaluated from the data shown in Fig's. 22 – 25 using linear regression of weighted data. The error bars indicated in Fig's. 22 – 25 were calculated from the instrumental uncertainties via error propagation from the transformation of *Celdeg* to ln(1/Y). Tab. 13 summarises the reaction rate constants obtained and their uncertainties.
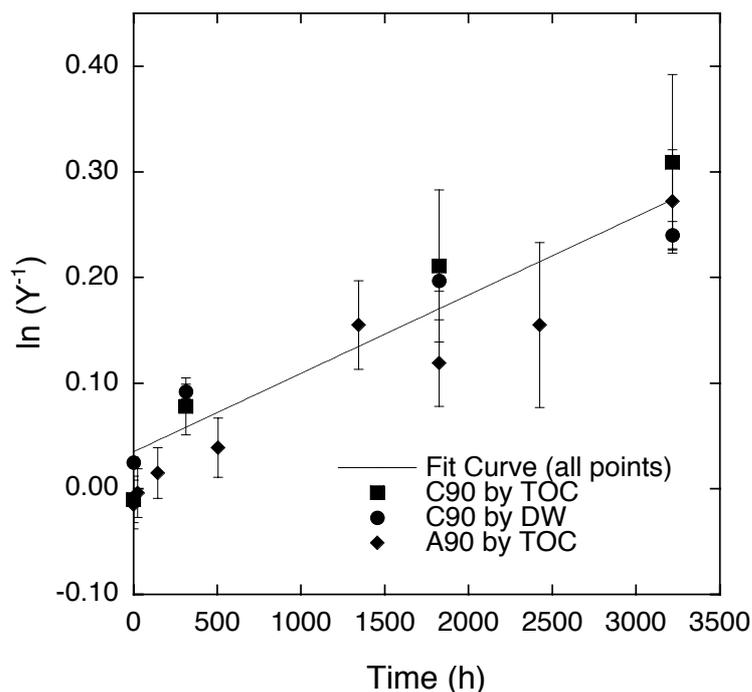

Fig. 22:

Evaluation of the "second reaction phase" (cf. section 4.1) for possible cellulose degradation through alkaline hydrolysis using selected data (corrected for peeling-off, cf. the text) from the degradation experiments of series A90 and C90 (Aldrich cellulose). Similar results are also obtained using the data from series B90-1.
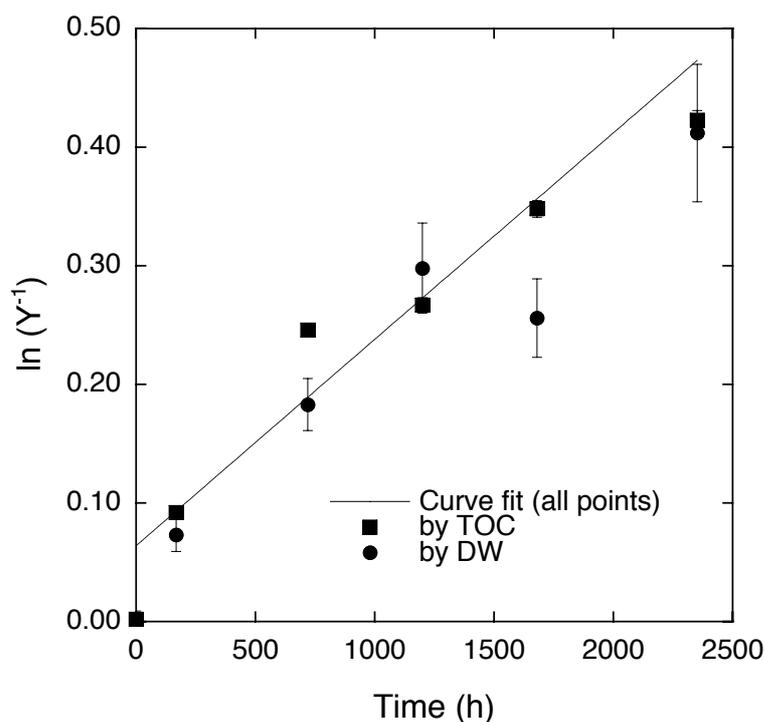
Fig. 23:

Evaluation of the "second reaction phase" (cf. section 4.1) for possible cellulose degradation through alkaline hydrolysis using selected data (corrected for peeling-off, cf. the text) from the degradation experiments of series E90 (cotton cellulose). Similar results are also obtained using the data from series F90.
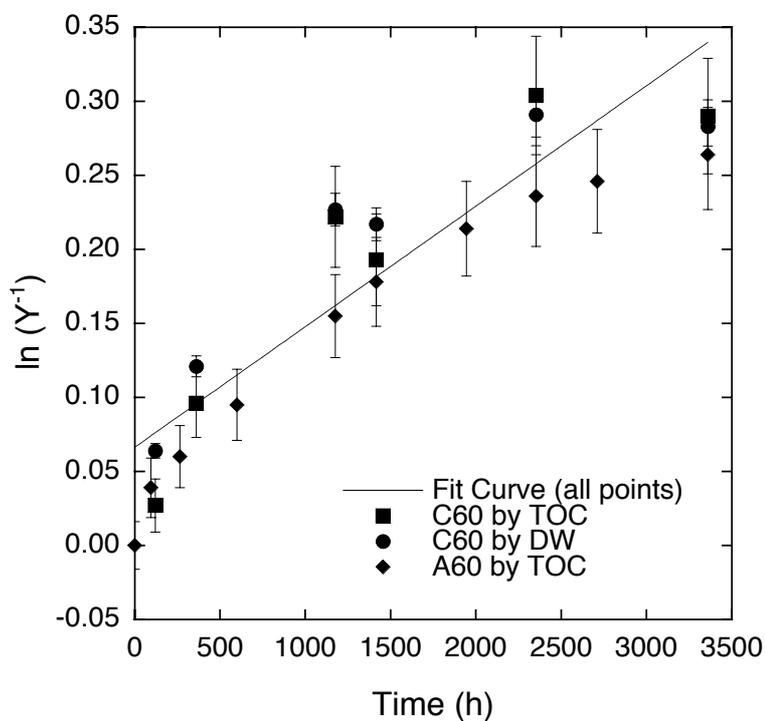
Fig. 24:

Evaluation of the "second reaction phase" (cf. section 4.1) for possible cellulose degradation through alkaline hydrolysis using selected data (corrected for peeling-off, cf. the text) from the degradation experiments of series A60-2 and C60 (Aldrich cellulose).
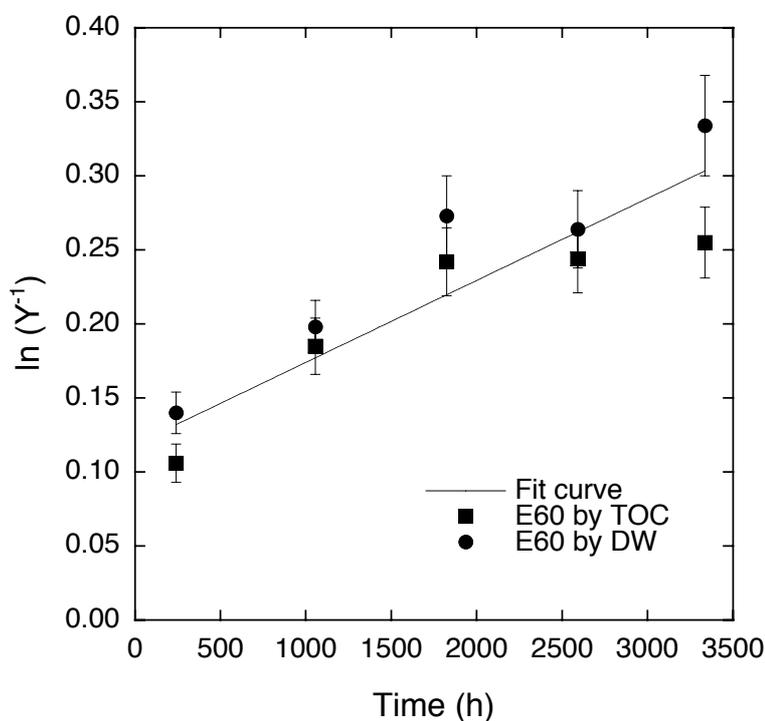
Fig. 25:

Evaluation of the "second reaction phase" (cf. section 4.1) for possible cellulose degradation through alkaline hydrolysis using selected data (corrected for peeling-off, cf. the text) from the degradation experiments of series E60 (cotton cellulose).

Tab. 13: Overview of the reaction rate coefficients (cf. eqn. (11)) calculated for possible alkaline hydrolysis based on the evaluations shown in Fig's. 22 – 25. Note that these reaction rate coefficients may not be indiscriminately used for model calculations, because they are only valid, if the reaction phase used to evaluate these constants represents actually alkaline hydrolysis of cellulose. This has to be regarded as a working hypothesis only.

Type of cellulose	Temp.	$k_{obs} = k'_{obs} \cdot \bar{x}_n$ (h^{-1})	$\bar{x}_n$ [a]	k'_{obs} (h^{-1})
Aldrich cellulose	90 °C	$(7.4 \pm 0.8) \cdot 10^{-5}$	69	$(1.1 \pm 0.6) \cdot 10^{-6}$ [b]
Cotton cellulose	90 °C	$(1.7 \pm 0.2) \cdot 10^{-4}$	140	$(1.2 \pm 0.6) \cdot 10^{-6}$ [b]
Aldrich cellulose	60 °C	$(8.1 \pm 0.8) \cdot 10^{-5}$	65	$(1.3 \pm 0.7) \cdot 10^{-6}$ [b]
Cotton cellulose	60 °C	$(5.5 \pm 0.9) \cdot 10^{-5}$	63	$(8.8 \pm 0.5) \cdot 10^{-7}$ [b]

[a] Evaluated from a representation of *Y* versus *Y*/(*DP*)$_t$ (FRANZON & SAMUELSON, 1957).

[b] Arbitrarily assuming a relative uncertainty of 50 % for $\bar{x}_n$.

4.2.2   Evaluation based on *DP*

FRANZON & SAMUELSON (1957) postulated a mathematical expression, which relates the *DP* at time *t*, *DP*$_t$, to the *DP* at time zero, *DP*$_0$ and *k*.

$$\ln\frac{DP_t + \bar{x}_n}{DP_t} = k \cdot t + \ln\frac{DP_0 + \bar{x}_n}{DP_0} \tag{12}$$

For given data pairs of *DP*$_t$ versus *t*, *k* may be optimised using *DP*$_0$ as a second adjustable parameter. This equation would principally offer the possibility to validate the parameters evaluated in the preceding section, because both *DP*$_t$ and *DP*$_0$ were not used for the assessment of *k*. One has to realise, however, that the mathematical structure of eqn. (12) leads to large uncertainties in the calculation of *DP*$_0$. For this reason, it is abstained in this report from this possibility of evaluation. Nevertheless, *DP*$_t$ is a very important parameter to be measured, in that it shows, whether mid-chain scissions actually take place in the experiments or not (cf. Fig's. 20 and 21).

4.3   Implications of the fit parameters obtained

A comparison between measured and extrapolated values for *k'* is given by Fig. 26. As can be seen from this plot, the values measured for 60 °C and 90 °C clearly deviate from the extrapolation made from the data of LAI & SARKANEN (1967) and FRANZON &

SAMUELSON (1957). Further, all values evaluated for *k'* within the frame of this work are identical within the range of experimental uncertainty. This findings strongly suggest that the reaction phase during which the "alkaline hydrolysis" has been evaluated is dominated by some unknown other degradation reaction different from alkaline hydrolysis. From the experimental evidence obtained in this work, it is not possible to conclusively identify this reaction. This interpretation, together with the observed stopping of the degradation reaction, is an indication that alkaline hydrolysis is too slow to be observed within the time span of these experiments. An indication that an unknown type of reaction is involved in the "second" reaction phase" can also be taken from the mass balance of carbon in solution. For the degradation of Aldrich cellulose at 60 °C (series A60-2), the sum of carbon concentrations of the reaction products analysed (α-ISA, β-ISA, glycolate, formiate, lactate, acetate) accounts for 97 % of TOC after 16 days of reaction (cf. Tab. 11). After a reaction time of 145 days, this figure decreases to 72 % and further to 65 % after 180 days. Similar conclusions can also be drawn from mass balances for carbon in the degradation of Aldrich cellulose at 90 °C, whereby the figures are in general lower than for the degradation at 60 °C (cf. Tab. 10).
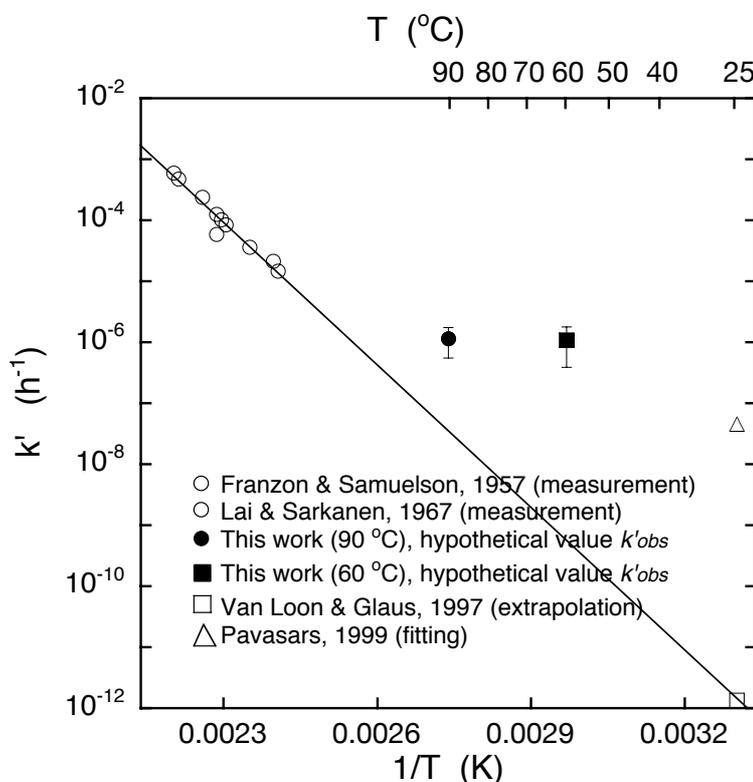
Fig. 26:

Summary of the various literature data for the re-action rate constant k' of the alkaline hydrolysis, as compared to the possible interpretation of the deg-radation reactions carried out in this work. Owing to the different values used for $\overline{x}_n$ the comparison is made using k'. The dis-crepancy between the extrapolation and the hy-pothetical values shows that alkaline hydrolysis has most probably not been observed in the present experiments.

This interpretation is also supported by literature data, in which the alkaline hydrolysis of methyl-β-glucoside has been measured in ~2.8 M NaOH and at temperatures between 140 °C and 170 °C (BROOKS & THOMPSON, 1966[11]). The resulting activation energy of 36 kcal·mol^{-1} is in good agreement with the slope found for the degradation of cellulose in the same temperature range (cf. Fig. 6). This shows that sterical and structural effects of the cellulose chain are not of importance at these high temperatures, as the ester linkage in methyl-β-glucoside is freely rotatable and not hindered in accessibility. However, the experiments carried out in the frame of the present work suggest, that such effects may become of importance in the intermediate temperature range. GENTILE et al. (1987) report that exposure of fibrous hydrocellulose to 1 M NaOH at 60 °C and 80 °C did not cause significant changes in accessibility of hydroxide ions. However, the time window of their experiments was restricted to one week at longest. Therefore, no direct conclusions from GENTILE et al. (1987) can be drawn for the experiments presented in this work.

For room temperature no such conclusion can be drawn, because the time span to observe such effects is too large with respect to the duration of experiments carried out so far (Van Loon & Glaus, 1998; Pavasars 1999; Hagberg, 2002).

4.4   Implications for the prediction of the long-term behaviour of cellulose

The proper purpose of this work — i.e. to increase the credibility in extrapolated values of *k'* applied in the calculation of the amount of cellulose degraded as a function of time — has thus not been satisfyingly fulfilled by the experiments carried out. A reliable extrapolation to room temperature can therefore not be made yet. The critical question — which cannot be answered within the scope of this work — is whether the unexpected "second reaction phase" observed at 60 °C and 90 °C is also of relevance for temperatures of ~25 °C. *In no way, the values of k'_{obs} presented in Tab. 13 should be indiscriminately used in a model of cellulose degradation for calculating the concentration of strong complexants in cement pore water.* Fig. 26 clearly shows that such values are lacking of a "reasonable chemical background".

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[11] Note that this work is erroneously referenced in Lai & Sarkanen (1967).

Because no models are available to account quantitatively for additional types of reaction, such as changes in physical structure of cellulose and accessibility of reactive groups, no realistic predictions for the degradation of cellulose in a cementitious environment can be made at the moment. It can only be speculated that the reaction rate constant for the alkaline hydrolysis at 25 °C is properly predicted by the extrapolation from the high temperature by the Arrhenius relation (VAN LOON & GLAUS, 1998). However, this model is not capable to explain the large degree of cellulose degradation observed in the case of cotton cellulose at 60 °C and 90 °C. Whether the processes responsible for these large degrees of cellulose degradation are also relevant for lower temperatures cannot be evaluated based on the present data.

In view of the many uncertainties of extrapolation, the prediction of cellulose degradation based on the reaction rate constants for the peeling-off process and alkaline hydrolysis as proposed by VAN LOON & GLAUS (1998) is probably — on the one hand —not on the safe side. However, a complete transformation of cellulose to strong complexants within a few years under repository conditions may be — on the other hand — an over-conservative assumption, when considering the fact that cellulose is not completely degraded at very high temperature and pressures (cf. e.g. NIEMELÄ & SJÖSTRÖM, 1986). Also in the present work strong evidences have been found for a complete stopping of cellulose degradation.

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APPENDIX: HPAEC AND HPIEC CHROMATOGRAMS

Representative HPAEC and HPIEC chromatograms are shown in the following. Slight differences in retention time may occur within one series, because these analyses may have been measured at different times. It is not possible to quantitatively compare the chromatograms within one series, because different dilution factors may have been applied to the samples.

MSA was only tentatively identified based on co-elution with a reference compound synthesised in our laboratory. The signal response for the detection of MSA is larger by a factor of ~50 than the response for ISA. For this reason the concentrations of MSA are not significant as compared to the concentration of the ISA isomers, and a quantitative evaluation of the peaks tentatively identified as MSA was carried not out.
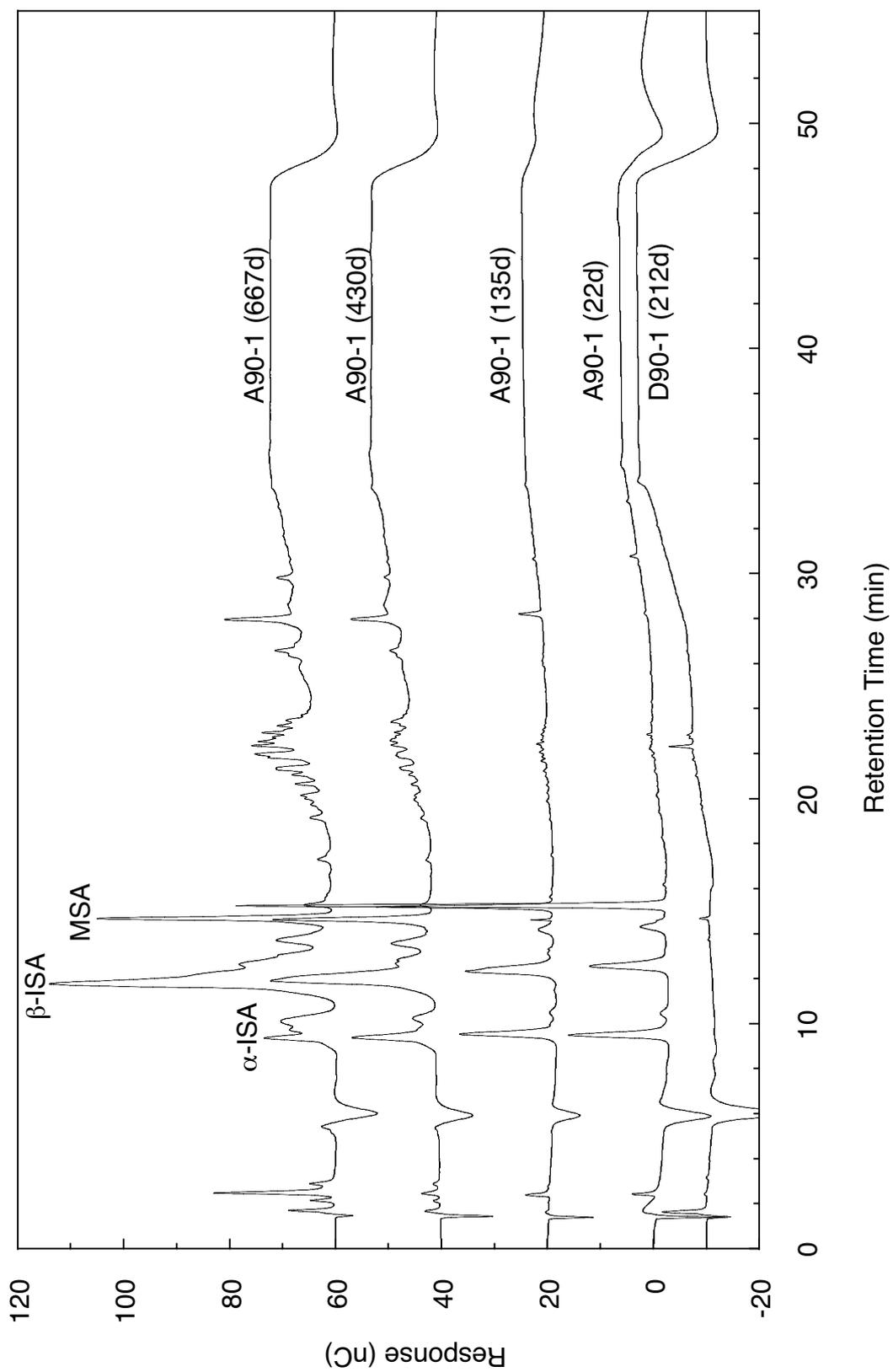
Fig. 27: HPAEC chromatograms of series A90-1.
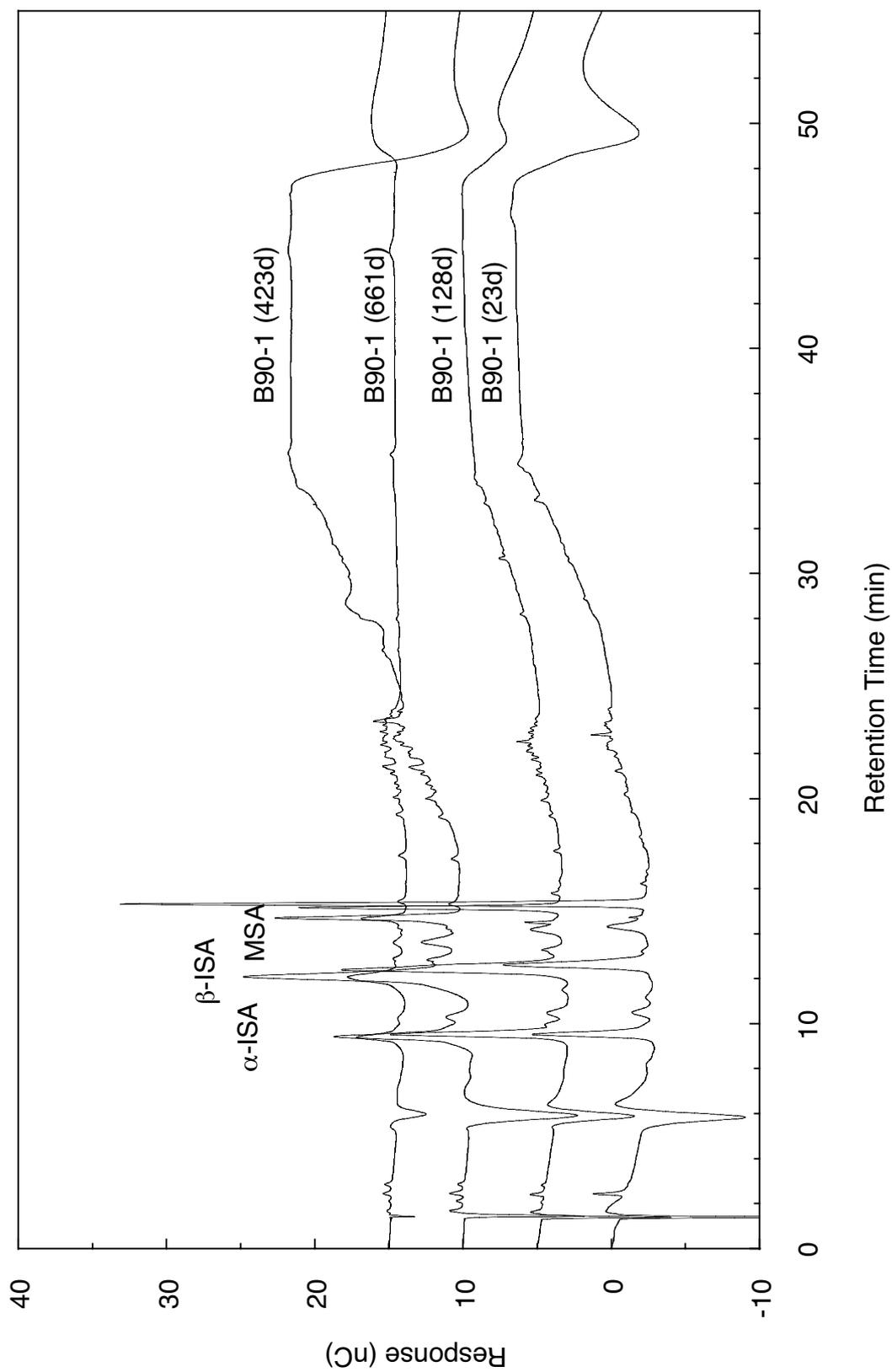
Fig. 28: HPAEC chromatograms of series B90-1.
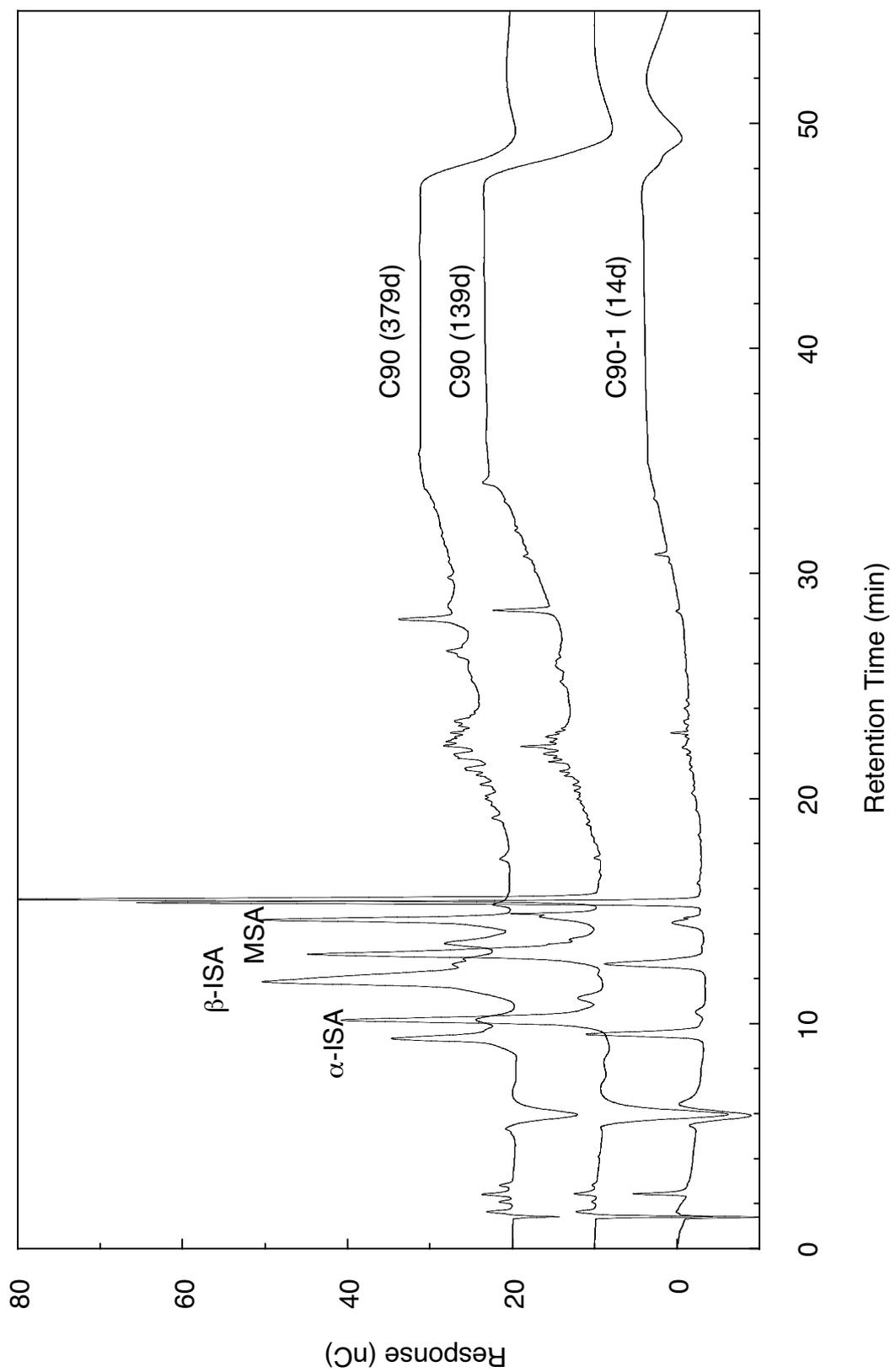
Fig. 29: HPAEC chromatograms of series C90.
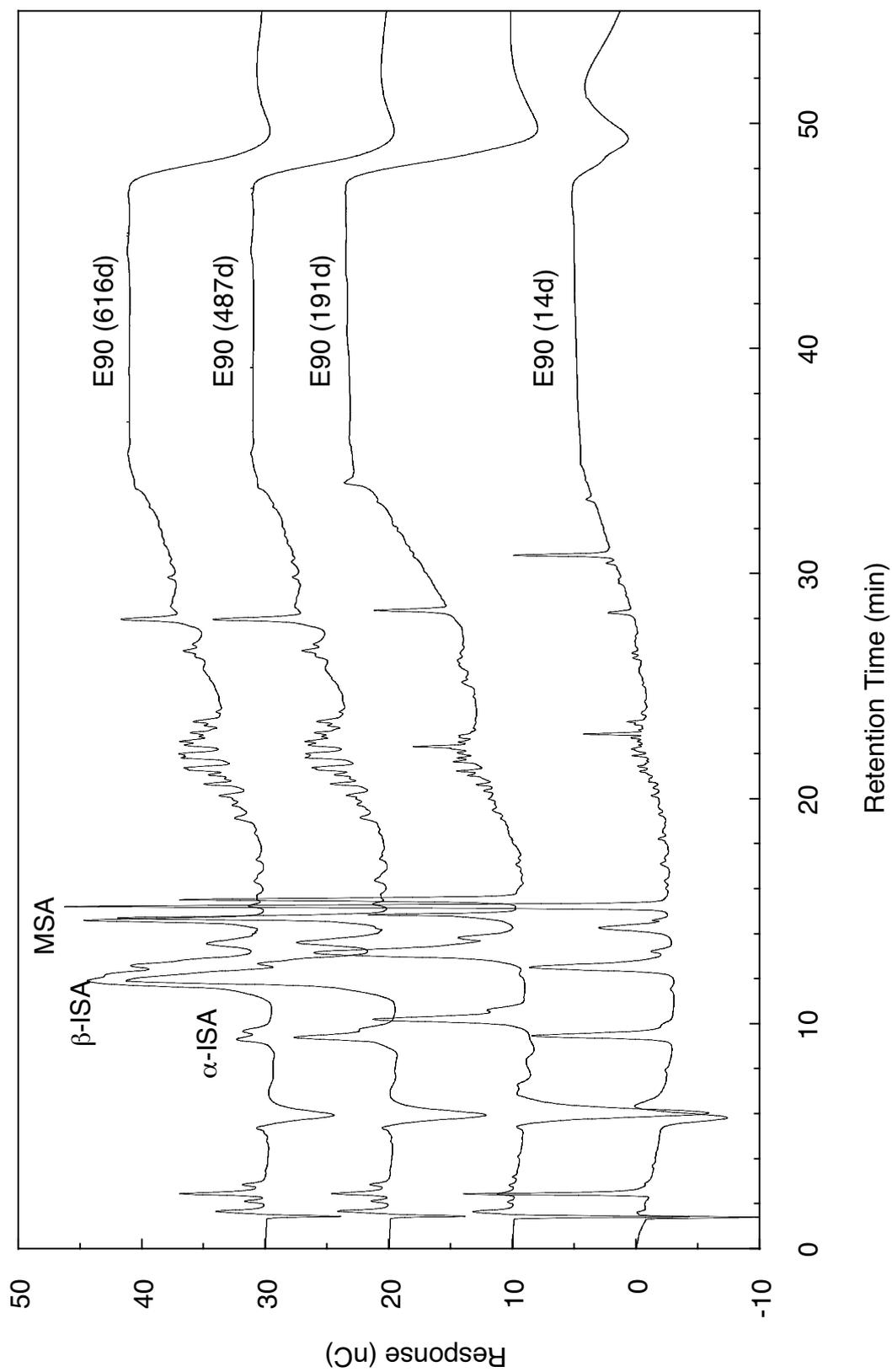
Fig. 30: HPAEC chromatograms of series E90.
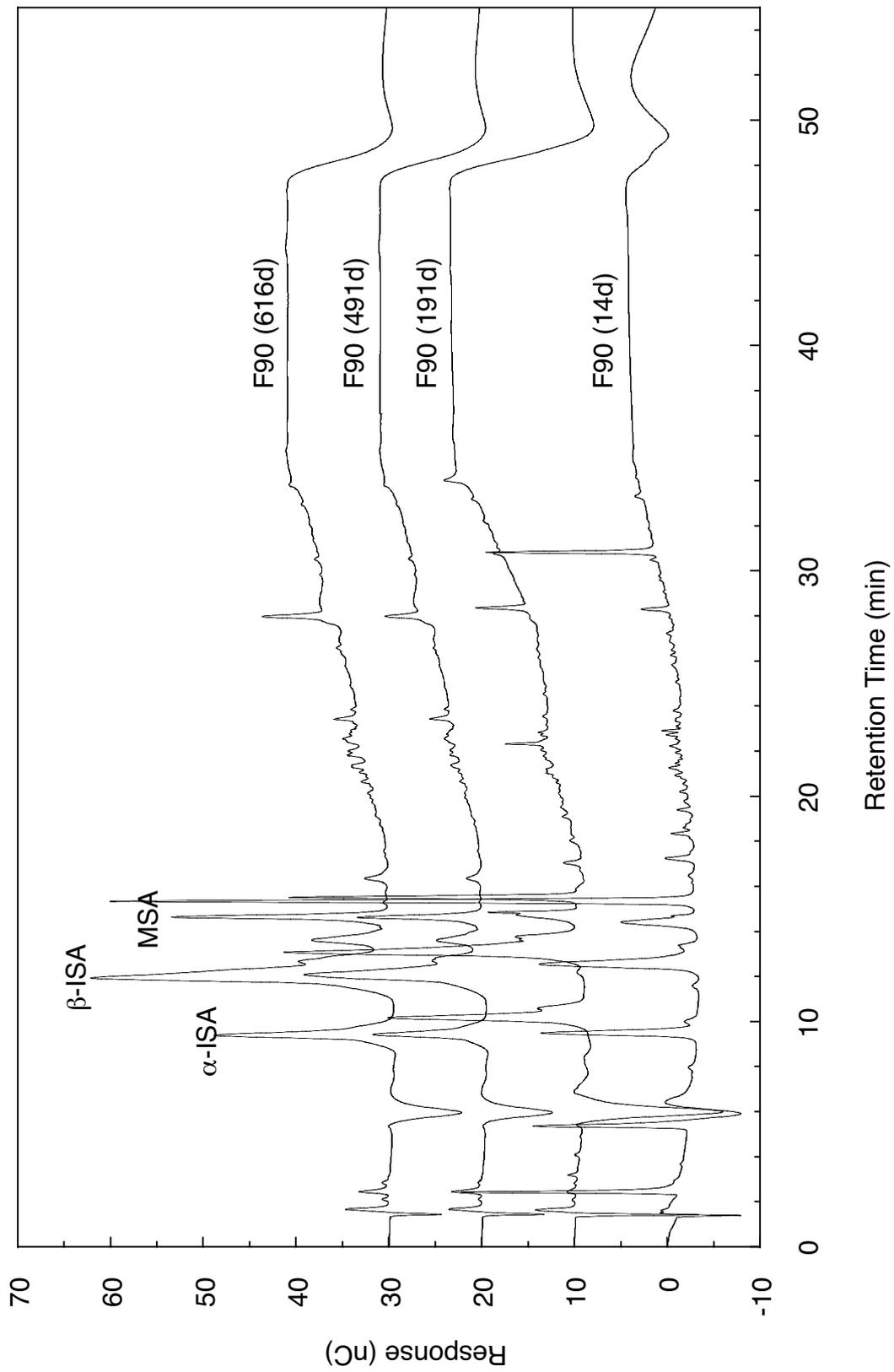
Fig. 31: HPAEC chromatograms of series F90.
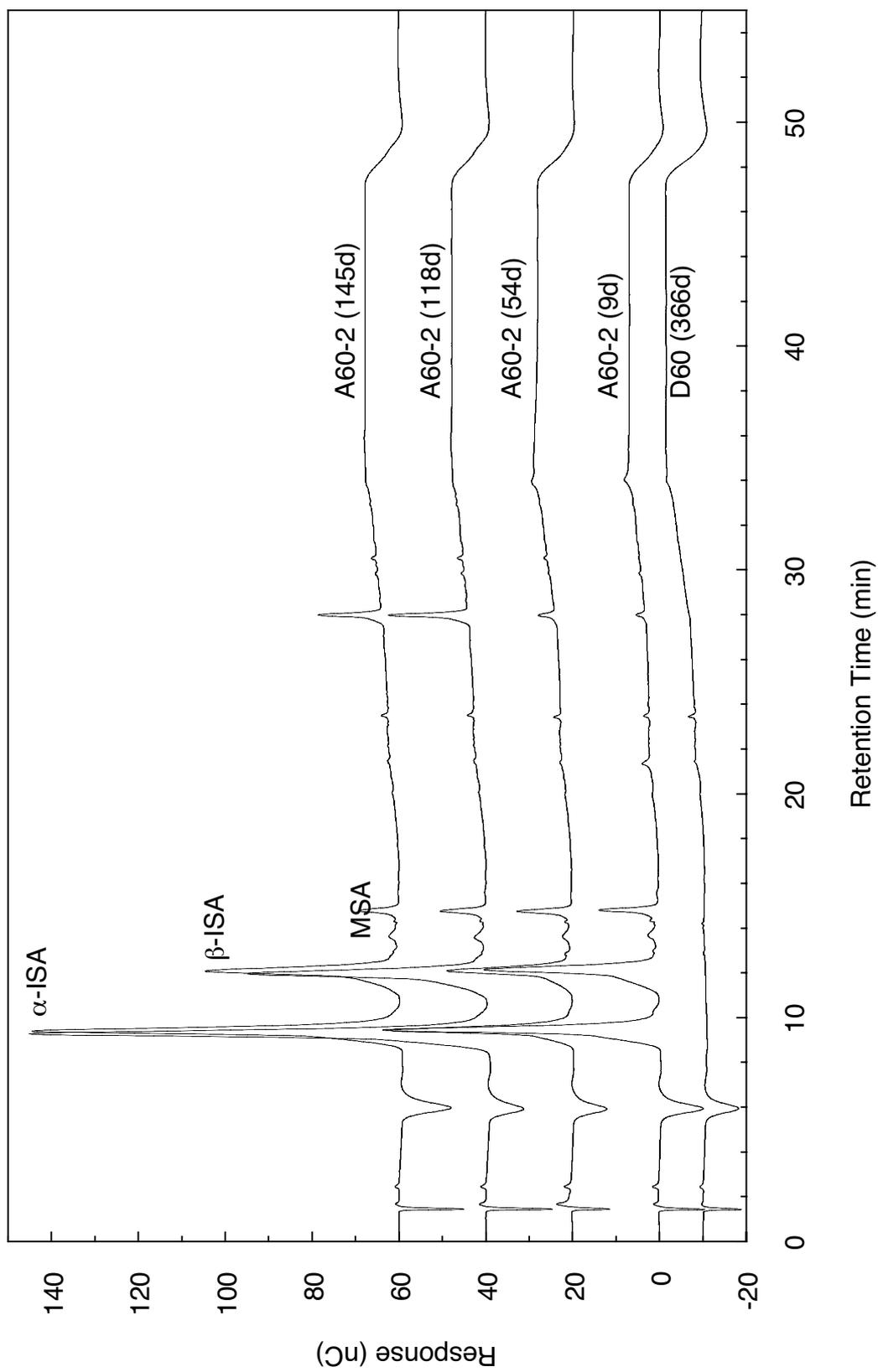
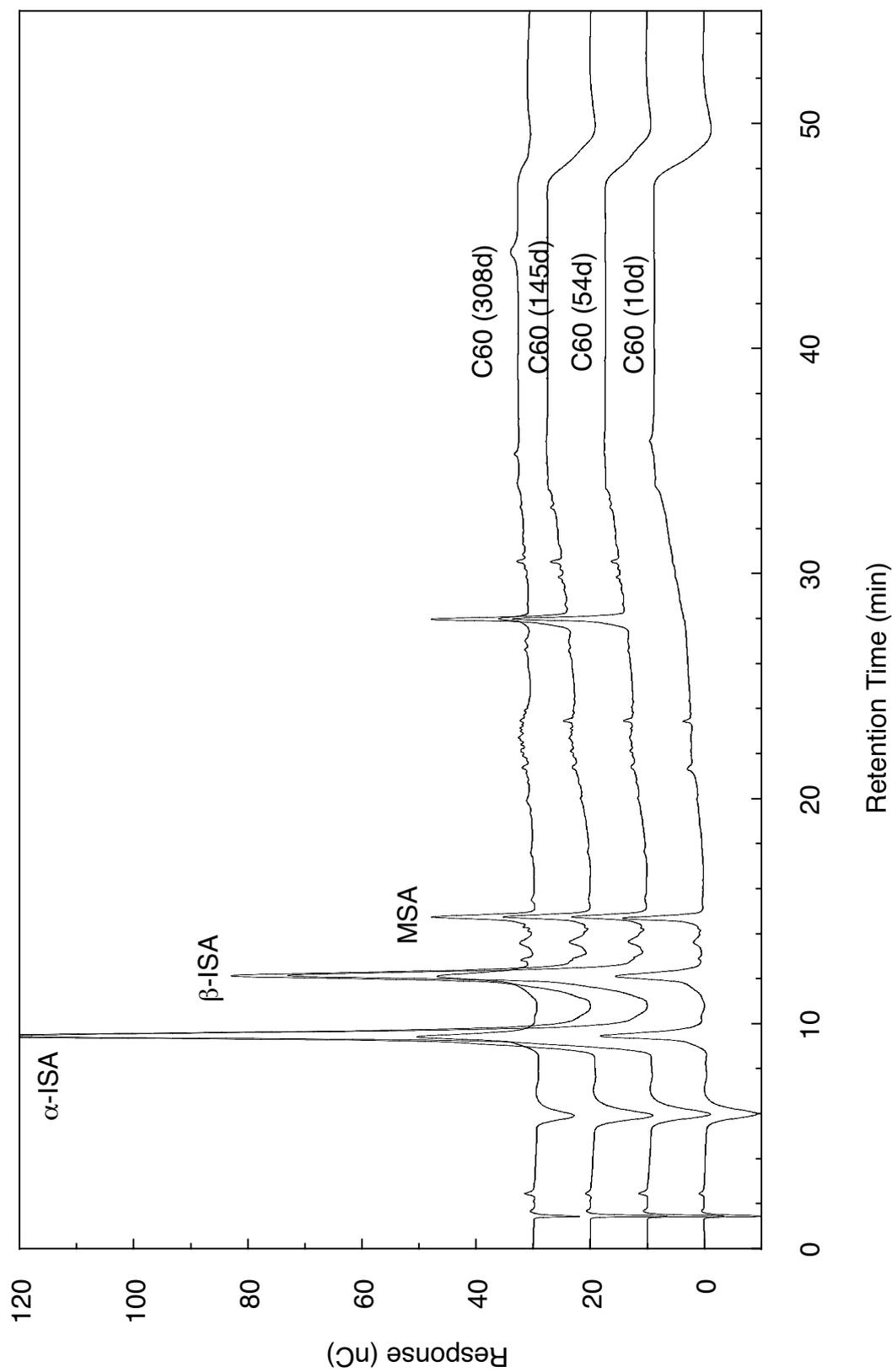*Fig. 32: HPAEC chromatograms of series A60-2.*
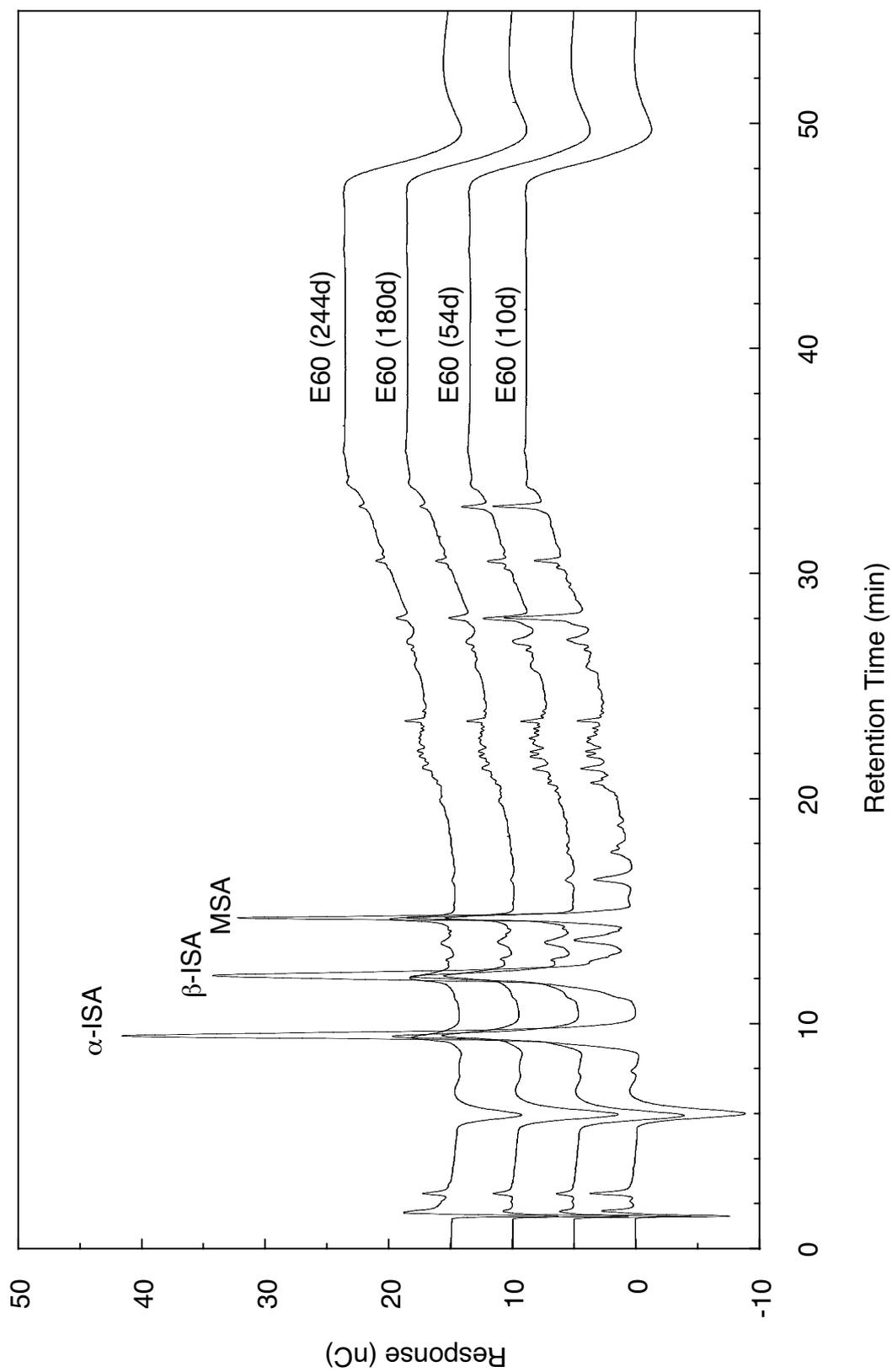
Fig. 33: HPAEC chromatograms of series C60.
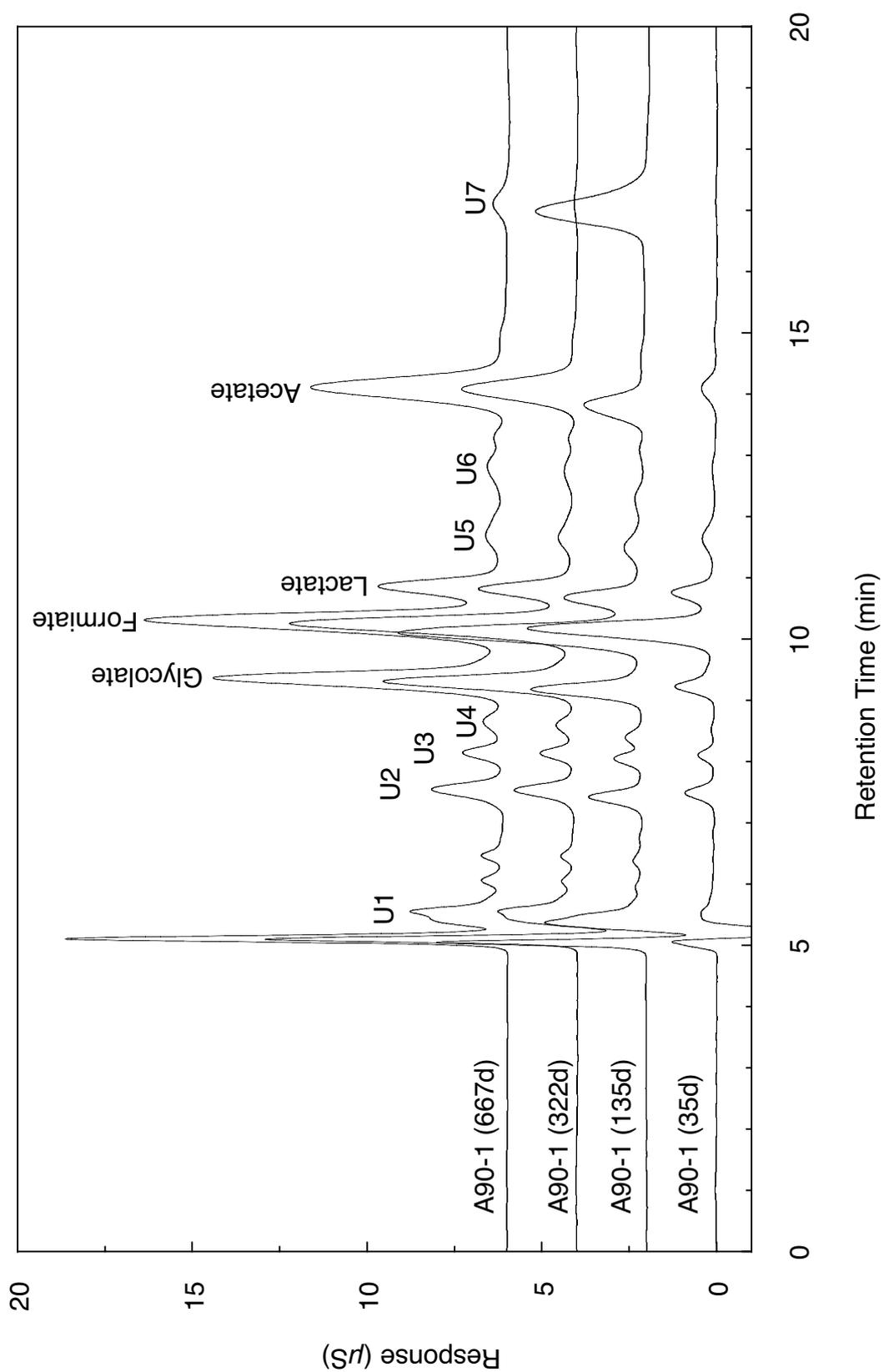
Fig. 34: HPAEC chromatograms of series E60.

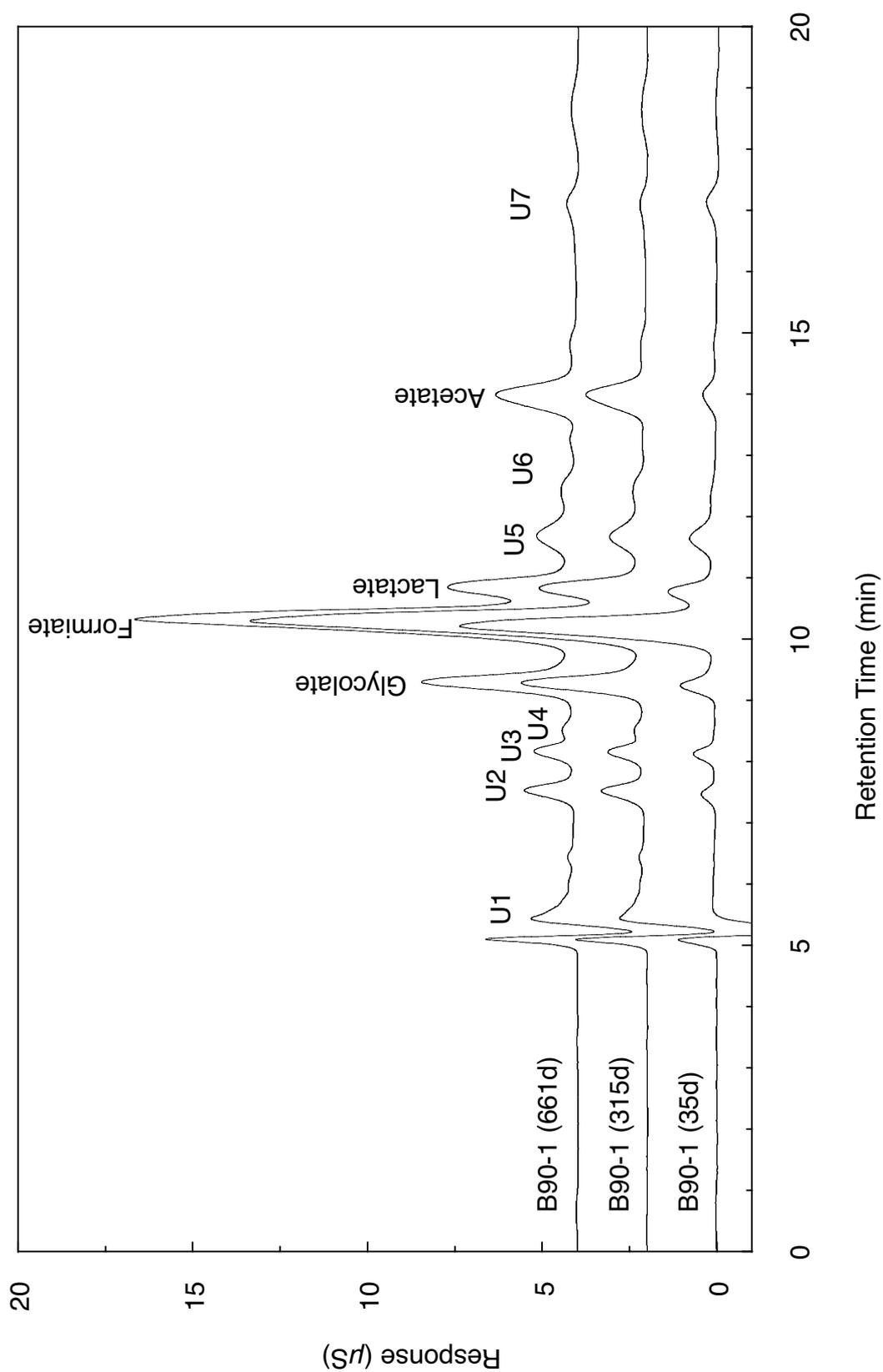Fig. 35: HPIEC chromatograms of series A90-1. Peaks denoted as 'Ux' are unknown compounds.

Fig. 36: HPIEC chromatograms of series B90-1. Peaks denoted as 'Ux' are unknown
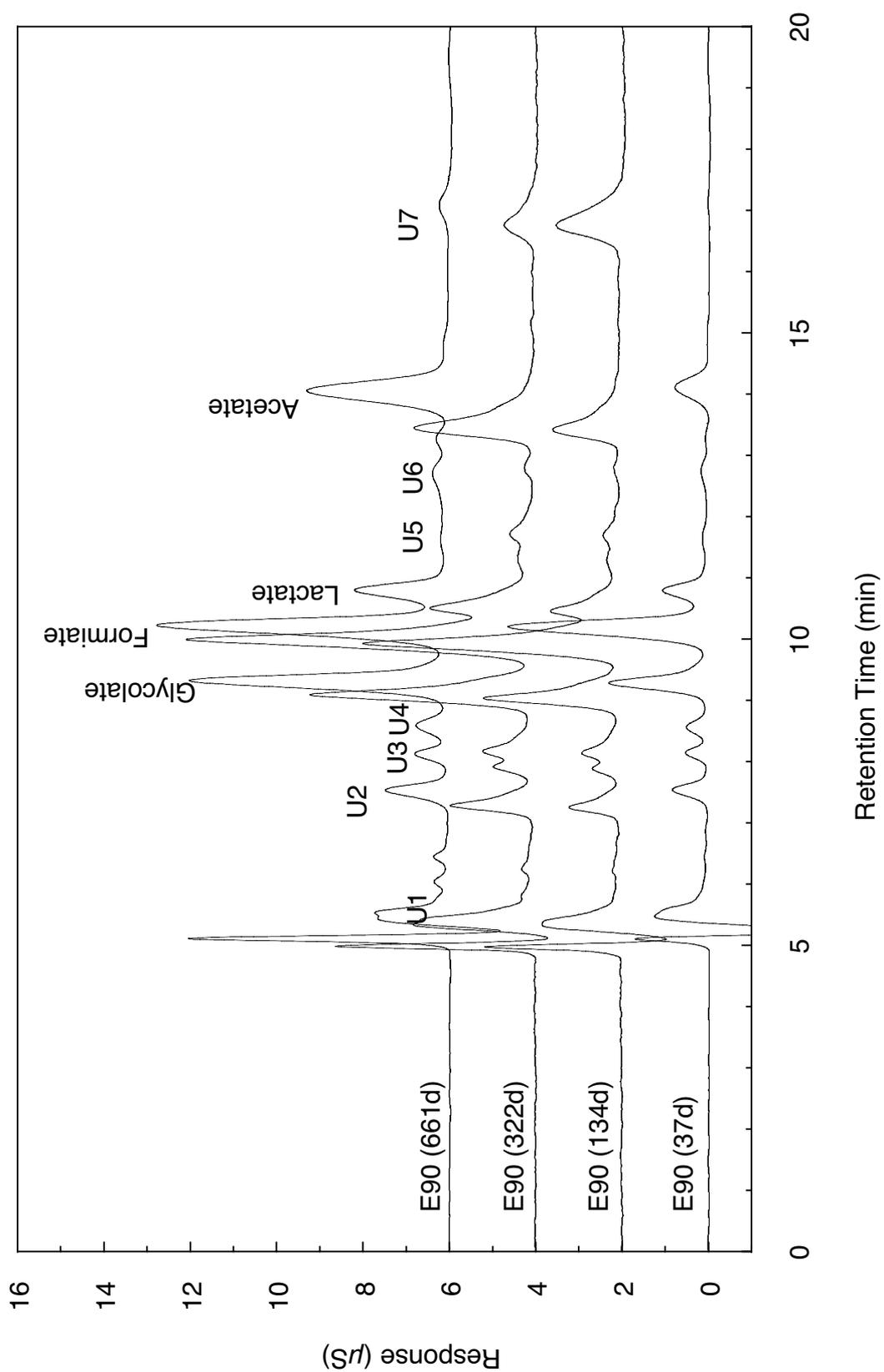compounds.

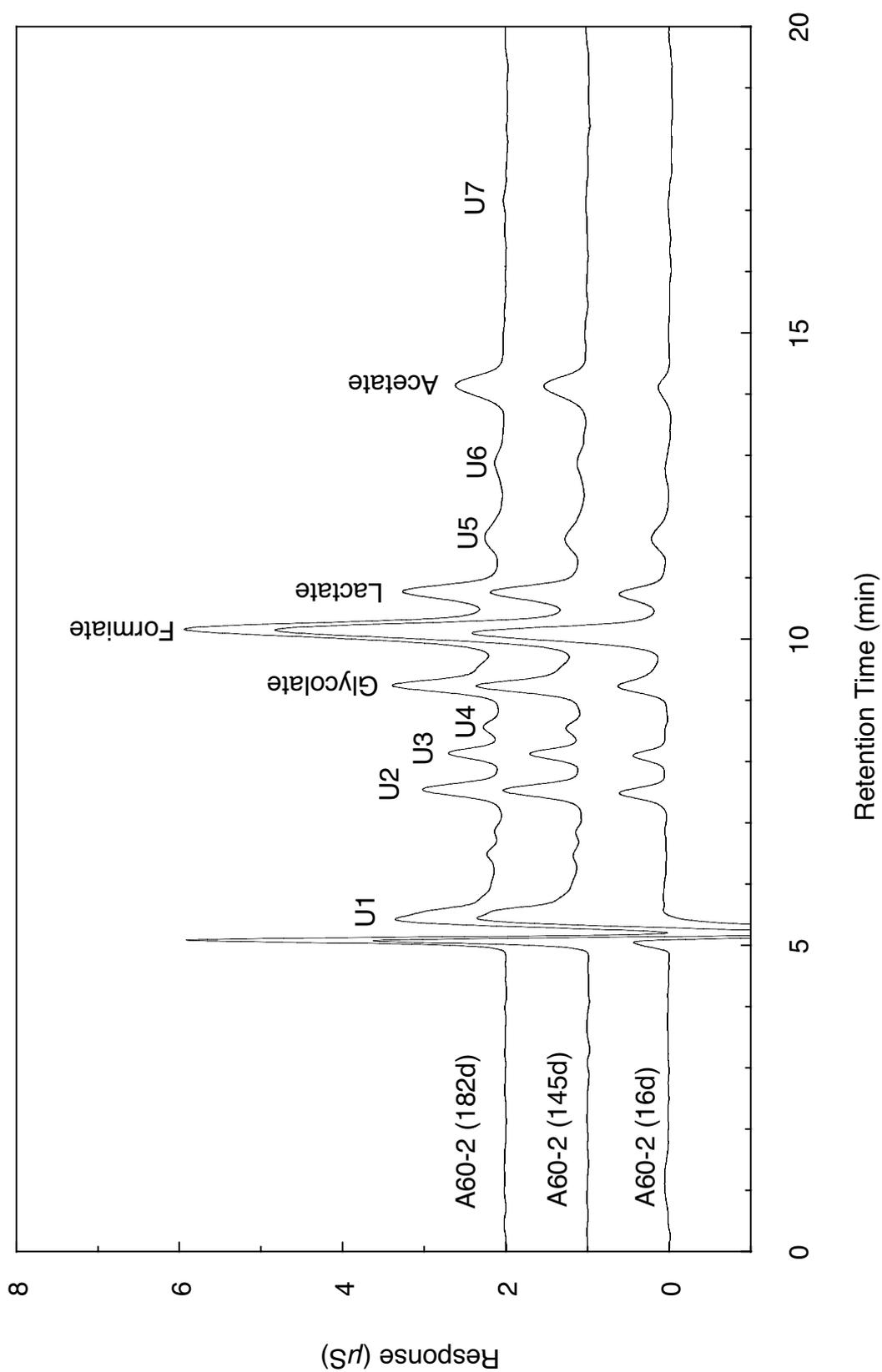Fig. 37: HPIEC chromatograms of series E90. Peaks denoted as 'Ux' are unknown compounds.

Fig. 38: HPIEC chromatograms of series A60-2. Peaks denoted as 'Ux' are unknown compounds.
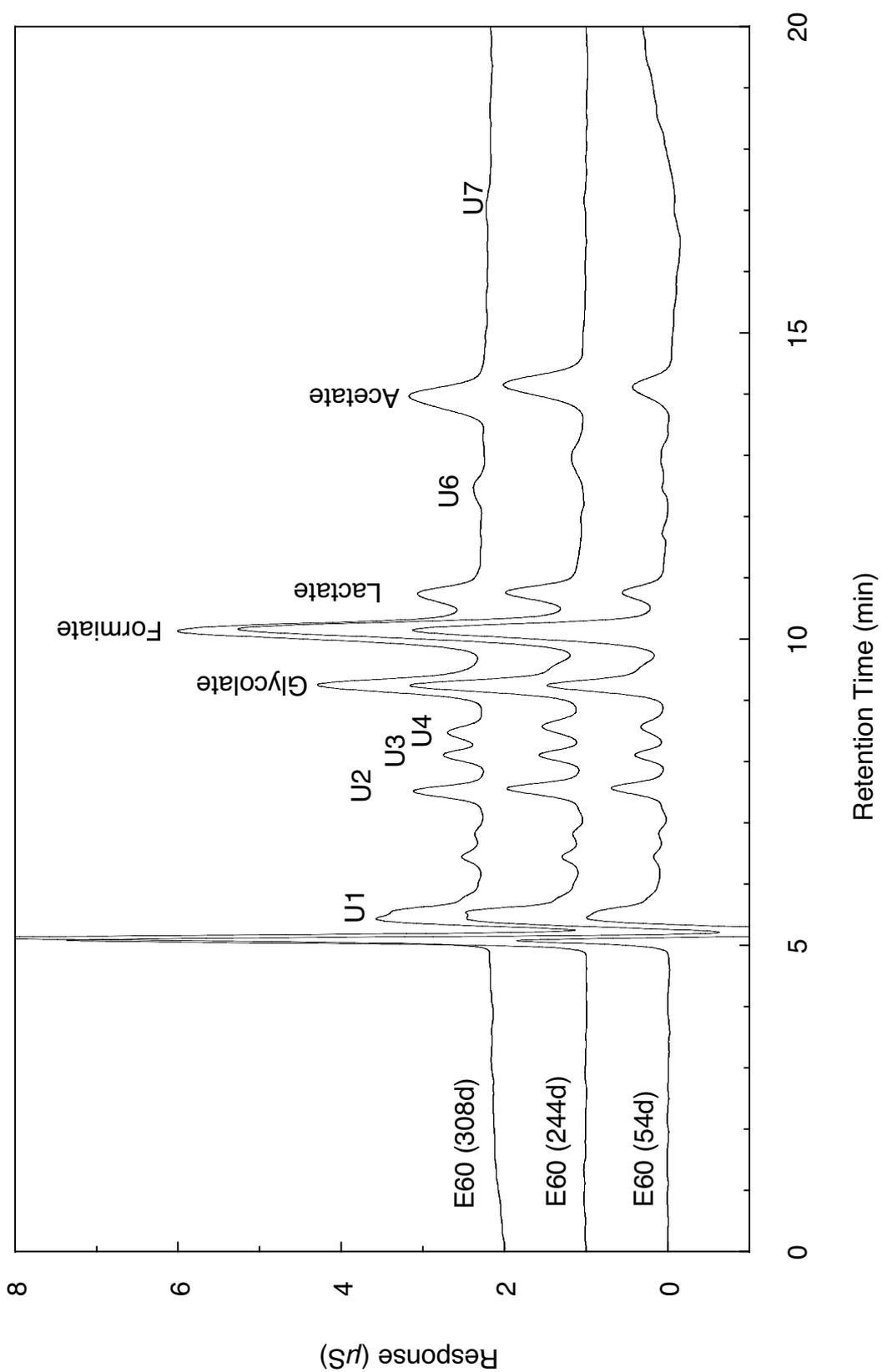
Fig. 39: HPIEC chromatograms of series E60. Peaks denoted as 'Ux' are unknown compounds.