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SUSTAINABILITY OF MASS DEACIDIFICATION OF LIBRARY OBJECTS

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Sustainability of mass deacidification of library objects

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Abstract

Mass deacidification treatment has been applied to books, in the libraries and archives, that were in jeopardy due to their acidity. Although it has been employed based on extensive research and tests, sustainability of mass deacidification was questioned due to lack of quality control systems and a risk of alkaline treatment to the original books, which have naturally aged for up to 150 years.

In the present study, the aims were not only the assessment of the performance of mass deacidification processes applied for the last two decades, but also the study of the influence of mass deacidification on a molecular level of cellulose, focusing on β -elimination triggered by alkali in combination with oxidative functionalities. Over 400 books from the German National Library and the Berlin State Library were analyzed. Surface pH was measured, and determination of alkaline reserve was carried out for selected original books by means of titration, X-ray fluorescence spectrometry (XRF), and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). Twenty-five deacidified books and their identical non-deacidified papers were analyzed by gel permeation chromatography (GPC) coupled with fluorescence and multiple angle light scattering detectors after fluorescence labeling of carbonyl groups, which offered deeper insights into degradation mechanisms of deacidified papers before and after accelerated aging.

Strictly speaking, according to the current Deutsches Institut für Normung (DIN) recommendations, mass deacidification that was applied to the books during 1994–2006 was not sufficient enough to meet the standards for pH and alkaline reserve for all the books measured. Variability in data of surface pH and alkaline reserve was brought about mainly by the deacidification processes and the year of publication.

The PapersaveTM process was found to perform relatively better than the others in terms of the amount of alkaline reserve as well as homogeneity. Fine and homogeneous distribution of alkaline reserve into the paper matrix as well as on the surface of the paper was found to be critical to enhance the efficacy of mass deacidification in the long run. The amount of alkaline reserve directly correlated with cellulose stability after accelerated aging, despite different conditions of the original book papers, which led to questions about the adequacy of current standards for the amount of alkaline reserve. Model book papers containing different amounts of alkaline reserve indicated that even an excessive amount of alkaline reserve did not completely cancel out the beneficial effect of alkaline reserve as a barrier against acidic attack.

β -elimination triggered by keto/aldehyde groups along the cellulose chain seems to be unavoidable after mass deacidification as well as during accelerated aging. However, thanks to the characteristic distribution of carbonyl groups found in naturally aged book paper, β -elimination did not cause severe chain scission to an extent that lowered the molecular weight. The study of accelerated aging added to this finding. Degradation of original deacidified paper was overruled by the benefits from alkaline reserve, reducing acid hydrolysis remarkably, without being affected severely by β -elimination. Degradation of cellulose after accelerated aging did not correlate with the initial carbonyl group content prior to accelerated aging or to the lowered content of along-chain carbonyls after accelerated aging, which is a sign of β -elimination. Therefore, a threat of alkaline degradation under conditions of the mass deacidification tested was minor.

Kurzfassung

In Bibliotheken und Archiven wurden Bücher, die infolge ihrer Acidität gefährdet waren, mit Massenentsäuerung behandelt. Obwohl diese Behandlung auf Grundlage umfangreicher Forschung und Tests angewendet wurde, wurde die Nachhaltigkeit der Massenentsäuerung aufgrund mangelnder Qualitätskontrollen und der Gefahr einer alkalischen Behandlung auf die originalen Bücher, die bis zu 150 Jahre natürlich gealtert waren, in Frage gestellt.

Die Ziele der vorliegenden Studie waren nicht nur die Beurteilung der Leistungsfähigkeit von Massenentsäuerungsprozessen in den letzten zwei Jahrzehnten, sondern auch die Untersuchung des Einflusses von Massenentsäuerung auf molekularer Ebene von Cellulose, fokussiert auf β -Eliminierung ausgelöst durch Alkali zusammen mit oxidativen Funktionalitäten. Über 400 Bücher aus der Deutschen Nationalbibliothek und der Staatsbibliothek zu Berlin wurden analysiert. Einerseits wurde der Oberflächen-pH-Wert gemessen, andererseits wurde die alkalische Reserve für ausgewählte Originalbücher mittels Titration, Röntgenfluoreszenz-Spektrometrie (XRF) und Rasterelektronenmikroskopie-Energie-Röntgen-Spektroskopie (REM-EDX) bestimmt. Fünfundzwanzig entsäuerte und ihre identen nichtentsäuerten Bücher wurden durch Gelpermeationschromatographie (GPC) mit Fluoreszenz- und Mehrwinkel-Laserlichtstreu-Detektoren nach Fluoreszenzmarkierung von Carbonylgruppen analysiert, wodurch eine besserer Einblick in den Degradationsmechanismus von entsäuerten Papieren, vor und nach beschleunigter Alterung, möglich war.

Entsprechend den derzeitigen Empfehlungen des Deutschen Institutes für Normung (DIN), war die Massenentsäuerung, die auf die Bücher zwischen 1994 und 2006 angewendet wurde, streng genommen nicht ausreichend, um die Standards für pH und alkalische Reserve für alle gemessenen Bücher zu erfüllen. Die Daten des Oberflächen-pH und der alkalischen Reserve variieren hauptsächlich durch die Entsäuerungsverfahren und das Publikationsjahr.

Das PapersaveTM Verfahren brachte bessere Ergebnisse als andere Methoden in Bezug auf die Menge an alkalischer Reserve sowie die Homogenität der Proben. Es wurde festgestellt, dass eine feine und homogene Verteilung der alkalischen Reserve sowohl in

der Papiermatrix als auch auf der Oberfläche des Papiers entscheidend für die Verbesserung der dauerhaften Wirksamkeit der Massenentsäuerung ist. Die Höhe der alkalischen Reserve

korreliert direkt mit der Cellulosestabilität nach beschleunigter Alterung, trotz unterschiedlicher Bedingungen der ursprünglichen Papiere, was die Angemessenheit der aktuellen Normen für die Höhe der alkalischen Reserve in Frage stellt. Modellbücher mit unterschiedlichen Mengen an alkalischer Reserve haben gezeigt, dass auch eine übermäßige Menge an alkalischer Reserve keine vollständige Barriere gegen sauren Angriff darstellt.

β -Eliminierung, ausgelöst durch Keto-/Aldehyd-Gruppen entlang der Cellulosekette, scheint unvermeidlich, sowohl nach Massenentsäuerung als auch während beschleunigter Alterung. Doch dank der charakteristischen Verteilung der Carbonylgruppen in natürlich gealtertem Papier verringert die Kettenspaltung durch β -Eliminierung das Molekulargewicht nicht in großem Ausmaß. Das wurde im Rahmen dieser Studie durch beschleunigte Alterung aufgezeigt. Der Abbau bei entsäuertem Originalpapier wurde durch die Vorteile der alkalischen Reserve aufgehoben, die saure Hydrolyse in bemerkenswertem Ausmaß reduziert, ohne stark durch β -Eliminierung betroffen zu sein. Der Abbau von Cellulose nach beschleunigter Alterung korreliert weder mit dem ursprünglichen Carbonylgruppengehalt vor der beschleunigten Alterung noch mit dem geringeren Gehalt von Keto-/Aldehyd-Gruppen entlang der Cellulosekette nach beschleunigter Alterung, was ein Zeichen von β -Eliminierung ist. Daher ist die Gefahr eines alkalischen Abbaus unter den Bedingungen der Massenentsäuerung nur gering.

List of publications

The following papers are part of this thesis:

- I. Ahn, K**, Henniges, U, Blüher, A, Banik, G & Potthast, A 2011, ‘Sustainability of mass-deacidification – Part I: Concept, selection of sample books, and pH-determination’, *Restaurator*, vol. 32, pp. 193-222.
- II. Ahn, K**, Banik, G & Potthast, A 2012, ‘Sustainability of mass-deacidification – Part II: Evaluation of alkaline reserve’, *Restaurator*, vol. 33, pp. 48-75.
- III. Ahn, K**, Henniges, U, Banik, G & Potthast, A 2012, ‘Is cellulose degradation due to β -elimination processes a threat in mass deacidification of library books?’, *Cellulose*, vol. 19, pp. 1149-1159.
- IV. Ahn, K**, Rosenau, T & Potthast, A 2013, ‘The influence of alkaline reserve on the aging behavior of book papers’, *Cellulose*, vol. 20, pp. 1989-2001.

List of other related publications

Ahn, K, Henniges, U, Banik, G & Potthast, A 2012, 'Nachhaltigkeit in der Massenentsäuerung von Bibliotheksgut', in R Altenhöner, A Blüher, A Mälck, E Niggemann, A Potthast & B Schneider-Kempf (eds), *Eine Zukunft für saures Papier*, Vittorio Klostermann, Frankfurt, pp. 29-87.

Henniges, U, Schiehser, S, **Ahn, K**, Hofinger, A, Geschke, A, Potthast, A & Rosenau, T 2012, 'On the structure of the active compound in mass deacidification of paper', *Holzforschung*, vol. 66, pp. 447–450.

Related oral presentation

Ahn, K, Henniges, U, Banik, G & Potthast, A 2011, 'Sustainability of mass deacidification of library objects', in International Conference-Renewable Wood and Plant Resources: Chemistry, Technology, Pharmacology, Medicine, Saint-Petersburg.

Potthast, A, **Ahn, K**, Blüher, A & Banik, A 2011, 'Fifteen years later: A study of the sustainability of mass deacidification: Practical implications', in IADA 7th International congress, August 29 – September 2, 2011, Berne, Switzerland

Potthast, A, **Ahn, K**, Jeong, MJ, Böhmendorfer, S & Rosenau, T 2012, 'New insights into aging of cellulosic materials', in EWLP, August 27-30, 2012, Espoo, Finland

Ahn, K, Becker, M, Jeong, MJ, Henniges, U, Zweckmair, T, Böhmendorfer, S, Rosenau, T & Potthast, A 2013, 'New insights into natural aging of biopolymers', in The 6th Separation and characterisation of macromolecules (SCM), February 6-8, 2013, Dresden, Germany

Related poster presentation

Ahn, K, Henniges, U, Blüher, A, Banik, G & Potthast, A 2010, 'Investigation of sustainability of mass deacidification treatments', in ICOM-CC Graphic documents working group – interim meeting, October 22-23, 2010, Copenhagen, Denmark

Ahn, K, Henniges, U & Potthast, A 2012, 'Is cellulose degradation due to β -elimination processes a threat in mass deacidification of library books', in 3rd International Cellulose Conference (ICC), October 10-12, 2012, Sapporo, Japan

Ahn, K, Henniges, U, Banik, G & Potthast, A 2013, 'Can alkaline reserve be harmful? In-depth studies into aging behavior of paper after mass deacidification', in Cultural heritage conservation science and sustainable development: experience, research, innovation. International conference in the frame of the 50th anniversary of CRCC, October 23-25, 2013, Paris, France

Abbreviations

AGU	anhydroglucopyranose unit
ANSI	American National Standards Institute
ATR	Attenuated total reflection
AR	Alkaline reserve
Avg	Average
CCOA	Carbazole-9-Carbonyl-Oxy-Amine
CSC	Conservacion de Sustratos Celulósicos
DEZ	Diethyl zinc
DIN	Deutsches Institut für Normung (German institute for standardization)
DMAc	<i>N,N</i> -dimethyl acetamide
DNB	Deutschen Nationalbibliothek (German National Library)
DP	Degree of polymerisation
DS	Degree of substitution
EDS or EDX	Energy dispersive X-ray spectroscopy
FDAM	Fluorenyldiazomethan
FT-IR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography mass spectrometry
GPC	Gel permeation chromatography
HMDO	Hexamethyldisiloxane
ICP	Inductively Coupled Plasma
ISO	International standardization organisation
KUR	Die Kulturstiftung des Bundes und die Kulturstiftung der Länder (German Federal Cultural Foundation and the Cultural Foundation of German States)
LA-ICP MS	Laser ablation inductively coupled plasma mass spectrometry
LODP	Leveling-off degree of polymerization
MALLS	Multiple angle laser light scattering
METE	Magnesium titanium ethoxide

Mn	Number average molecular weight
MS	Mass spectrometer
Mw	Weight average molecular weight
MW	Molecular weight
MWD	Molecular weight distribution
Mz	z-average molecular weight
NCW	Nitrochemie Wimmis AG
OES	Optical emission spectrometry
PAL	Preservation academy GmbH, Leipzig
PDI	Polydispersity index
PTFE	Polytetrafluoroethylene
PTI	Preservation Technologies, Inc.
R ²	Coefficient of determination
REGs	Reducing end groups
RH	Relative humidity
RI	Refractive index
RMS	Root mean square
RSD	Relative standard deviation
SBB	Staatsbibliothek zu Berlin (Berlin State Library)
SD	Standard deviation
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SN EN	Schweizer Norm Europäische Norm (Swiss standard European standard)
SNL	Swiss National Library
TAPPI	Technical Association of the Pulp and Paper Industry
TRI	Total Risk Indicator
UV	Ultraviolet
XRF	X-ray fluorescence
ZFB	Zentrum für Bucherhaltung

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1. Introduction

1.1. Background and objectives

Paper is mainly composed of cellulose, which is the most abundant natural polymer in nature. Unlike the handmade paper in the early era of paper-making history, modern paper-making methods contributed dramatically to the formation of acids in paper, leading to severe deterioration of paper that can eventually no longer function as an information carrier. To solve this problem, mass deacidification treatments have actively been applied to collections of libraries and archives in Europe and North America since the 1990s. Mass deacidification aims, on a kilogram to ton scale, to neutralize existing acids in paper and to introduce an alkaline reserve to prevent degradation from acids, which resume formation in subsequent aging processes.

After about two decades of application of mass deacidification, continuation of the treatments faced questions. Some of them are related to a lack of systemized quality control standards and procedures, and some of them originate from fundamental issues connected to alkaline treatments. The questions are: Have the books been treated properly? If not, what are main causes? What do the quality standards indicate for the beneficial effects that mass deacidification brings about? Can any preservative effects of the treatment be observed from the books treated more than 10 years ago? What are the long-term effects of mass deacidification on the molecular level of cellulose of the original objects that have been treated so far? Can any adverse effects of the treatment be found in the cellulose structure of the treated books?

It is evitable to address these matters not only to continue the treatments, ensuring a good quality, but also to improve the processes and the quality control methods.

Thanks to a program established by the Federal Cultural Foundation and the Cultural Foundation of German States (Die Kulturstiftung des Bundes und die Kulturstiftung der Länder, KUR) and the cooperation of the German National Library (Deutsche Nationalbibliothek, DNB), the Berlin State Library (Staatsbibliothek zu Berlin, SBB), and the Swiss National Library (SNL) in Bern, the present study was carried out to answer those questions within the following work frames.

- Assessment of quality of mass deacidification processes applied in the 1990s and 2000s by means of surface pH and three different methods of examination of

alkaline reserve.

- Investigation of major causes for fluctuation of the pH and alkaline reserve.
- Study of direct effects of mass deacidification on the molecular structure of cellulose.
- Study of long-term effects of alkaline reserve left in paper by analyzing degradation mechanisms of cellulose during accelerated aging compared to identical book paper not treated.
- Examination of interrelation between surface pH, alkaline reserve, and molecular weight and carbonyl groups of cellulose.

1.2. Acids in paper

Alum-rosin sizing is known to be responsible for a low pH found in historic book paper. To make the fiber surface hydrophobic enhancing printability or writability, alum-rosin sizing has been applied in paper mills from the 1840s until the 1980s (Barrow Research Laboratory 1974). Alum in a form of potassium aluminum sulfate ($\text{KAl}(\text{SO}_4)_2$) or aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) was an essential ingredient to fix rosin, as a free acid or in saponified form, to cellulose (Roberts 1996). However, a side product was sulfuric acid, which made paper very acidic.

Atmospheric pollutants such as sulfur dioxide or nitrogen oxides also cause an increase in paper acidity, especially in margin areas (Bégin et al. 1999; Havermans & Steemers 2005). Nitrogen dioxide influences mechanical properties of paper more severely than sulfur dioxide or ozone (Adelstein et al. 2003). Lignin and alkaline reserve play a role in increasing absorption rates of air pollutants (Atherton et al. 1973; Banik et al. 1993; Gurnagul & Zou 1994; Guttman & Blair 1996; Johansson et al. 2000; Zou et al. 1998; Zou 2004; Daniel et al. 1990). Concerning general paper properties, lignin enhances discoloration in the presence of air pollutants, whereas alkaline reserve makes paper resistant against strength loss induced by air pollutants.

Beside atmospheric pollutants or paper-making parameters, organic acids can also be generated by cellulose degradation itself. Low molar mass organic acids, e.g., acetic acid and formic acid, can originate from carbohydrate fragments produced from cellulose by cleavage of the glycosidic bond and subsequent degradation and oxidation steps;

however, detailed mechanisms are missing. Acetic acid especially is often used as a marker of degradation of paper (Strlič et al. 2007; Doering 2007). Emission of relatively high molar mass carboxylic acids such as octanoic and decanoic acids from naturally aged groundwood paper were also reported (Lattuati-Derieux et al. 2004; Pedersoli Jr. et al. 2011). Shahani and Harrison (2002) could detect acetic, formic, lactic, oxalic acids, etc., only after several months of natural aging. Vanillic acid was found in particularly lignocellulosic paper (Dupont et al. 2007). Photochemical oxidation of lignin and hemicellulose can contribute to an increase of carboxylic groups in the molecular structure (Carter 1989). Acids formed via degradation of cellulosic materials seem not to significantly contribute to lowering the pH of paper or to degradation of cellulose unless they are accumulated to high concentration, since they are usually weak acids (Porck & Teygeler 2001). Recent studies revealed that the influence of acetic acid vapor on paper is not very significant, while formic acid vapor can negatively affect cellulose stability (Potthast et al. 2012; Tetreault et al. 2012; Di Pietro & Ligterink 2012).

Due to the internal and external causes of acids elaborated briefly above, the majority of books published in the 19th–20th centuries were found to be acidic; 80–90% of the books at the Slovak National Library published in the 20th century displayed a pH lower than 5 (Hanus et al. 2006); most of books of the Swiss National Library in Bern were below pH 6 before the deacidification treatment (Grossenbacher 2006, p. 9 fig. 3); 93% of books in the Royal Library in Denmark were acidic (Hansen & Vest 2008); Barrow Research Laboratory measured an average pH below 5 for book paper published in the 18th–20th centuries (Barrow Research Library 1974, as cited by Brückle 1993); a survey of over 20,000 books in Poland showed that almost 100% of books were acidic for the books published between the 1930s and the 1980s (Baranski et al. 2005).

1.3. Mass deacidification

Since the concept of deacidification of paper was issued by Schierholtz (1936) and Barrow in the 1930s (Roggia 2001), the deacidification treatment has been applied frequently in paper conservation workshops. Application of alkaline earth bicarbonates or hydroxides in an aqueous medium or simple washing with water was studied first for small to large conservation workshops, and was described in numerous literatures (Kelly

1989; Arney et al. 1979; Tang & Jones 1979; Williams 1979; Williams 1981; Brederick et al. 1990; Lienardy & Van Damme 1990; Bansa 1998; Bogaard & Whitmore 2001; Moropoulou & Zervos 2003; Bogaard et al. 2005; Stephens et al. 2009; Smith 2011). Deacidification technologies have been evolved toward non-aqueous deacidification systems remarkably since Baynes-Cope (1969) and Smith (1970) first introduced the application of barium oxide in methanol and of carbonated magnesium methoxide in methanol, respectively. Nonaqueous deacidification methods have been developed on a mass scale, since they meet the needs of libraries and archives, where tons of books have to be deacidified. Compared to aqueous deacidification, nonaqueous deacidification can minimize swelling of paper so that a whole book with water-sensitive inks and colors can be treated. A variety of combinations of active alkaline substances and carrier solvents of nonaqueous deacidification methods have been tested such as methyl magnesium carbonate in methanol (Kelly et al. 1977; Green & Leese 1991), gaseous diethyl zinc (Williams & Kelly 1976), various amine compounds in vapor phase (Kusterer & Hind 1972; Kusterer & Spoull 1973; Walker 1977) or in liquid phase (Koura & Krause 1980; Rousset et al. 2004), and micro-size magnesium oxide suspended in halogenated hydrocarbons (Kundrot 1985). Among those methods, some of them were developed successfully on a large scale and will be explained below in more detail.

Mass deacidification processes can be classified according to the carrier medium, the deacidification agent, and the type of treatment: aqueous liquid immersion, nonaqueous liquid immersion, nonaqueous liquid suspension, and dry application of submicron particles.

Mass deacidification processes generally carried are based on four steps: drying (preconditioning), deacidification (treatment), postdrying (postconditioning), and reconditioning. Drying (preconditioning) is to reduce the moisture content of paper, generally under vacuum and/or moderate heat or using freeze drying. It will enhance the uptake of reagent and lower the extent of moisture-driven side reactions. The actual deacidification is an impregnation step, transporting the active agent into the paper. The neutralization of acids present in paper commences in this step. Apart from the LibertecTM process, all mass deacidification processes available at present immerse whole stacks of books to increase the penetration of active alkaline agent into the paper

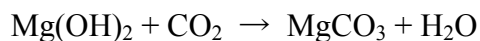
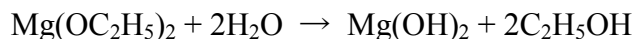
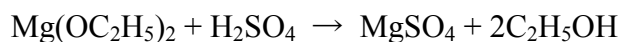
in the solution or suspension. The postdrying step is necessary to remove residual solvent and other volatiles, often under vacuum. Finally, the reconditioning step involves formation of alkaline reserves, recovery of the ambient moisture content of the paper, and extra evaporation of volatiles, e.g., alcohols, that are produced during the impregnation of alkaline reserve. This step is carried out with extra humidification or in an open environment at ambient condition.

1.3.1. PapersaveTM process (formerly “Battelle”) and PapersaveTM Swiss process

Battelle Ingenieurtechnik GmbH (previously the Battelle Institute) in Frankfurt started its development with the German National Library (Deutsche Nationalbibliothek) in 1987 (Porck 1996; Wittekind 1994). After a period of technical investigations, a combination of nonaqueous deacidification reagents, magnesium titanium ethoxide (METE) dissolved in hexamethyl disiloxane (HMDO), was developed. Battelle claims that HMDO is inert and nontoxic and reduces the risk of ink or color bleeding compared to an alcoholic carrier (Wittekind 1994). In addition, it possesses a relatively low viscosity with low surface tension, which enhances the uptake rate of the deacidification reagent (Wittekind 1994; Liers & Schwerdt 1995). The first installation and operation was carried out in the Deutsche Bücherei, Leipzig, in 1994 (Porck 1996), and currently, two operation sites are available: Battelle Ingenieurtechnik (Battelle) in Eschborn, Germany, and Zentrum für Bucherhaltung (ZFB) in Leipzig, Germany. Its third-generation process, called the Papersave SwissTM, started operation by Nitrochemie Wimmis AG (NCW) in Switzerland in 2000. It applies the exact same principle of deacidification as the PapersaveTM process, but has improved variability of process control parameters and the reconditioning process (Blüher & Vogelsanger 2001). Procedures of the PapersaveTM process are well described by Liers and Schwerdt (1995) and Porck (1996), although the detailed parameters might have been changed over optimization of the process.

The following reactions are expected to take place during the PapersaveTM process and the PapersaveTM Swiss process: reactions of titanium ethanlates and titanium isopropanolates are accompanied, forming mainly titanium dioxide, of which NCW takes advantage as an internal standard for analysis of alkaline reserve by XRF (Blüher &

Vogelsanger 2001; Andres et al. 2008).

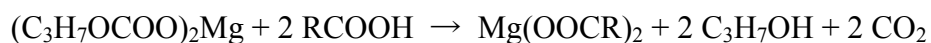


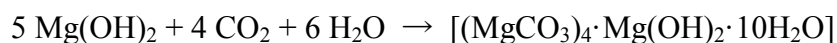
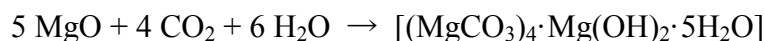
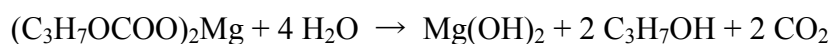
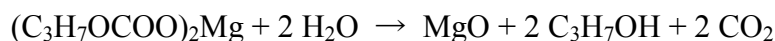
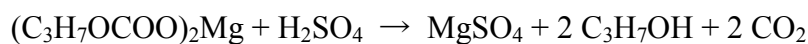
ZFB presented the outcome of the PapersaveTM process with pH 7–9 and 0.5–2.0% of alkaline reserve (Lichtblau & Anders 2006). Currently, they assure pH 7–9.5 and 0.5–2.0% of MgCO₃ based on the DIN recommendations (Hofmann & Wiesner 2011) (ZFB 2012). NCW and its current major customers, Swiss National Library and Swiss National Archive, presented satisfactory results of five years of operation of the Papersave SwissTM process, pH 7–10, MgCO₃ by XRF of 0.5–1.6%, meeting their internal quality standards (Blüher 2006; NCW 2004; Reist 2006; Grossenbacher 2006). Also, good penetration of alkaline reserve into the paper matrix (Ramin et al. 2009) and reduction of cellulose degradation in the treated paper after accelerated aging (Andres et al. 2008) were demonstrated.

1.3.2. CSC Book SaverTM process

The CSC Book SaverTM pilot plant was built in Spain by Conservacion de Sustratos Celulósicos (CSC) in 1999, using a newly developed deacidification technique patented by Dr. Areal Guerra Rogelio and his colleagues (2001). In 2003, another operational site was established by the Preservation Academy GmbH (PAL) in Leipzig, Germany, to provide the service directly to libraries and archives in Central Europe. The Russian National Library in St. Petersburg also operates the process in-house, under the supervision of PAL. This process applies carbonated magnesium propylate in *n*-propanol dissolved in a liquefied gas 1,1,1,2,3,3,3-heptafluoropropane (HFC 227) as deacidification agent. It claims a relatively low water sensitivity of the reagent, which allows shortening of the operation time (Banik 2004).

The following reactions are expected to occur depending on the environment, especially the availability of water in the atmosphere (Henniges et al. 2012).





Examination of test batches of the CSC Book SaverTM process resulted in a range of pH 8.2–9.1 and 0.3–0.8 % of alkaline reserve (Banik 2004). Relatively homogeneous deposition of alkaline reserve in the paper matrix was presented by Ramin et al. (2009). A spray product, the CSC Book SaverTM reagent for single sheets of paper, also showed positive effects in terms of protecting paper from NO₂ (Dupont et al. 2002).

1.3.3. BookkeeperTM process

Preservation Technologies, Inc. (PTI, previously Koppers Company Laboratories) was established in 1992 in Pennsylvania, U.S., to supply the BookkeeperTM process based on Kundrot's patent (1985). Since 1995, evaluation, optimization, and improvement of the process had been carried out mainly with the Library of Congress in Washington, D.C., and it has been applied to the books and the archives of the Library of Congress until the present (Pork 1996; Library of Congress n.d.a). At the same time, the National Library of the Netherlands obtained satisfactory results from the BookkeeperTM process as well, presumably influencing the establishment of a service provider of the BookkeeperTM process, Archimascon B.V. (Preservation Technologies purchased this company in 2010) in the Netherlands. The BookkeeperTM process is currently available worldwide, with facilities in the Netherlands, Canada, Spain, Poland, and Japan. The BookkeeperTM process utilizes a unique concept of deacidification, i.e., a suspension of submicron particles of magnesium oxide in perfluoro-heptane with assistance of a surfactant. Since the active reagents are not dissolved, agitation during the immersion is necessary to disperse the suspension more efficiently. Direct deposit of magnesium oxide allows the process to work without preconditioning and with only 24 hours of reconditioning in an open environment after removal of excess suspension (Preservation Technologies 2012). When it is applied to a single sheet of paper in the form of a spray, it seems that the penetration of alkaline reserve in the paper matrix is not complete (Ramin et al. 2009) and needs extra humidification (Boone et al. 1998).

1.3.4. LibertecTM/SOBUTM process

Libertec Bibliothekendienst GmbH in Nürnberg, Germany, developed another process that mainly applies magnesium oxide as a deacidification agent, like the BookkeeperTM process in the early 1990s (Porck 1996). Instead of any solvent carrier, it employs a dry stream of air that blows magnesium oxide and calcium carbonate onto the paper (Libertec n.d.). Its liquid-free procedures bring about no risk of ink or color bleeding or any side effects that can be caused by immersion in an organic solvent, and it requires no preconditioning step. The target amount of alkaline reserve is already determined by measuring the weight and surface roughness of the book (Pork 1996; Libertec n.d.). Since it deposits magnesium oxide on the surface of the paper, it requires humidification at around 30 °C to generate magnesium hydroxide and to induce penetration. Test application of the process was carried out for the collection of the Berlin State Library in the late 1990s. The process has been available via Libertec Bibliothekendienst in Nürnberg, Germany, but current operation is not known. The diffusion process of the active alkaline substances into the paper matrix as well as efficient transformation to magnesium hydroxide or magnesium carbonate are questionable (Zumbühl & Scherrer 2003; Blüher 2006), which means its long-term effects on paper are unknown.

1.3.5. BückebugTM process

The BückebugTM process was developed in the early 1990s for the State Archives in Bückebug, Germany, (Porck 1996). It is a unique mass deacidification process in terms of the carrier of the active deacidification agent, as it is an aqueous immersion system. To protect water-sensitive inks or dyes on paper, it applies ionic fixatives such as Rewin EL® (cationic) or Mesitol NBS® (anionic), which were successfully tested on the scale of conservation workshops (Blüher et al. 1999). By immersing single paper sheets in a solution of magnesium bicarbonate, neutralization of acids and impregnation of the deacidification agent take place. Extra strengthening of paper by means of methyl cellulose also makes it different from other processes. GSK GmbH (formerly Neschen AG in Germany) provides several types of compact machines for operating the BückebugTM process, which can be installed in-house or used as a service (GSK 2013a). Schempp Bestandserhaltung GmbH in Germany is also available for the service. Due to

the use of a water-immersion technique, an entire book cannot be treated. Thus it is only applicable to single sheets of paper. Preselection of items, removal of metal components, and a flattening step after the treatment are additional work required, compared to nonaqueous systems (Lojewski 2012). Groundwood containing newsprint, after deacidification with this process, showed about 26% loss of ultimate strength after 12 years of natural aging, whereas the untreated control lost 42% (Höing 2008).

1.3.6. Other processes and new trends in mass deacidification

Beside the processes described previously, the Wei T'oTM process has been actively applied to collections of libraries in Canada since the 1980s (Porck 1996). Methoxy magnesium methyl carbonate (MMMC) dissolved in methanol and hydrochlorofluorocarbons are employed by the process.

The SableTM process that shares operation principles with the Wei T'oTM started its application to the collection of the French National Library in Paris in 1989 (Valls 1993). The Viennese process was developed combining calcium hydroxide deacidification with a consolidation treatment with methyl cellulose, to strengthen newspapers in the Austrian National Library in Vienna (Porck 1996; Wächter 1987). Graft copolymerization processes also aimed at strengthening of paper in addition to alkaline reserve, using graft copolymerization of acrylic polymers onto cellulose by gamma radiation (Shenton 2006). The British Library was involved in this development, but it never reached more than a pilot scale of operation (Shenton 2006). The DEZ (Akzo) process that used diethyl zinc in the gas phase at reduced pressure, and the FMC process, of which the active agent was MG-3 (magnesium butoxytriglycolate) (Brandis 1994), were also operated on a pilot scale and are no longer available (Blüher & Vogelsanger 2001).

The ZFB:2TM process using particles of calcium carbonate and magnesium oxide dispersed in nonpolar solvents like heptane was introduced in 2011 (Anders 2011). It is claimed that the particles of alkaline substances are small enough to penetrate the paper matrix and that a risk of high pH can be reduced due to the use of calcium carbonate.

The PapercareTM process is also in progress of being applied. Supercritical carbon dioxide technology is involved in this process. It is expected to enhance paper strength immediately, due to the deacidification agent used ((aminoalkyl) alkoxy silanes), which polymerizes within the paper in addition to increasing pH (Blankenborg & Havermans

2010). GSK mbH in Brauweiler, Germany, which provides the BückebergTM process, also launched a novel process in 2010—the Book CP process—for deacidification of books (GSK 2013b). The process uses a combination of decafluoropentane, magnesium oxide, and magnesium carbonate and offers CO₂ gassing for better distribution of the suspension of active substances and extra cleaning on top of consolidation with ethyl cellulose (GSK 2013b).

The latest deacidification methods have been evolving toward application of nanoparticles of alkaline earth hydroxide (Giorgi et al. 2005) or impregnation with alkali using supercritical carbon dioxide (Ikonnikov et al. 2010).

Bibliography and patents on mass deacidification are available in the literature: Mihram 1986a and 1986b; Lienardy 1991; Zimmerman 1991; Porck 1996; Morrison 1979; Brandt 1992; Cedzova et al. 2006; Baty et al. 2010; and Adams 2011, to name a few.

1.4. Alkaline degradation of cellulose

Although numerous studies have proven that the life expectancy of paper increases after alkaline treatment compared to untreated paper in general, the question of whether paper undergoes alkaline-induced cellulose degradation due to the treatment remains unclear. A risk still exists, because the papers to be treated at libraries and archives have aged naturally for up to 150 years. Hydrolytic and oxidative degradation have occurred in the paper prior to the deacidification, increasing a risk of alkaline degradation induced by the treatment. This chapter will discuss alkaline degradation of cellulose, elaborating the feasibility of alkaline degradation in relation to the condition of aged paper.

1.4.1. Peeling reaction (endwise depolymerization)

Cellulose chain cleavage can occur due to the presence of the reducing end groups as glucopyranose hemiacetals under alkaline conditions. It eventually leads to loss of one anhydroglucose unit at the chain end at a time, as indicated by its other names, “peeling” reaction or “endwise” depolymerization (Fengel & Wegener 1984; Lai 2001). Enediol intermediates are first formed by isomerization of the reducing end group, by the so-called Lobry de Bruyn–Alberda van Ekenstein rearrangement. Then the

C-4-substituent, which is in β -position to the anionic intermediates, is cleaved off, resulting in a new reducing end of the chain (Lai 2001) (Fig. 1-1). The remaining compound forms a dicarbonyl structure by tautomerization. Since it is unstable under alkaline conditions, it forms isosaccharinic acid by a benzilic acid rearrangement or 2,5-dihydroxypentanoic acid by Cannizzaro type disproportionation reactions (Sjostrom 1977; Fengel & Wegener 1984). As the eliminated unit contains a new reducing end group, this β -elimination reaction can be initiated again under alkaline condition and will be repeated, shortening the chain gradually.

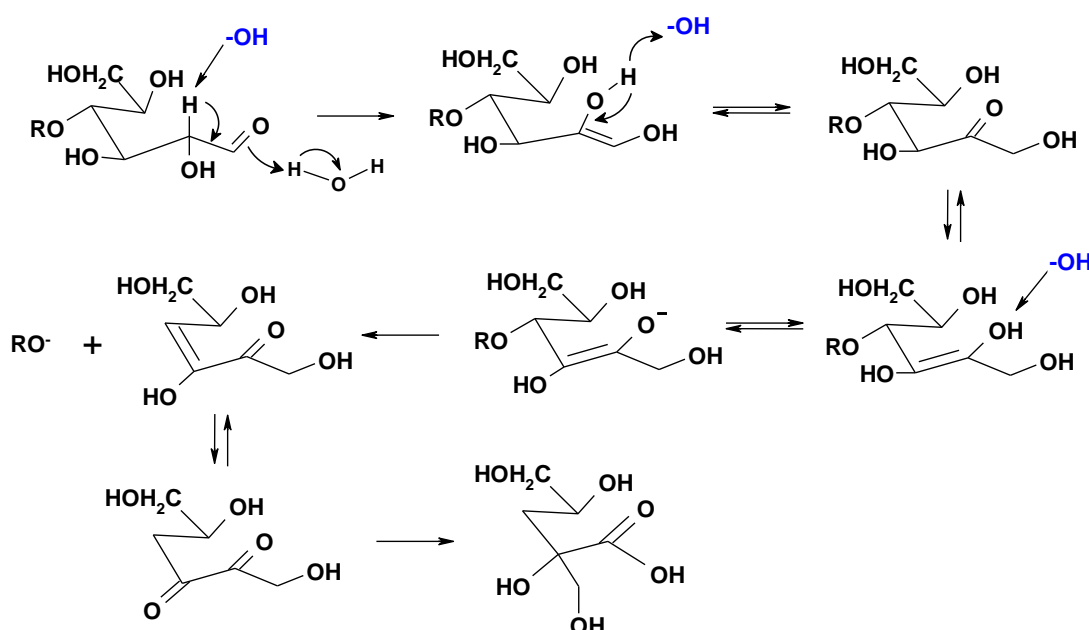


Fig. 1-1. Peeling reaction under alkaline condition (Potthast 2006).

However, the peeling reaction can be terminated by forming stable acids such as metasaccharinic acid or 2-C methylglyceric acid after enolization of the reducing end group or when it reaches crystalline regions (Haas et al. 1967). Otherwise, the reducing end groups should be reduced to alcohol or oxidized to carboxylic groups to stop or minimize the peeling reaction. If the C2-OH group is substituted, the endwise peeling reaction cannot proceed.

As a result of the peeling reaction, approximately 50–60 glucose units are generally peeled off before a stopping reaction (Fengel & Wegener 1984; Franzon & Samuelsson 1957; Lai & Sarkanen 1967). Even if it happens in the deacidified paper, its influence is

rather negligible, taking into account an average DP_w of cellulose of 1500 of naturally aged book papers, according to the 28 books analyzed. In addition, the peeling reaction proceeds with a significant rate only at elevated temperatures, above approximately 100 °C (Fengel & Wegener 1984, p. 296). According to a recent study, the reaction rate of peeling increases more than thirteenfold under alkaline pulping conditions when the temperature goes up from 125 °C to 160 °C, demonstrating the large temperature dependency of this reaction (Testova et al. 2013). In case of immersion systems in mass deacidification, heating can be involved in the preconditioning (drying) step and removal of a solvent carrier right after impregnation of the deacidification agent. However, it hardly exceeds 60 °C during the preconditioning step (Liers & Schwerdt 1995). Thus, the peeling reaction does not occur to any large extent under the conditions of a mass deacidification treatment.

1.4.2. β -elimination triggered by keto and aldehyde groups along the cellulose chain (oxidative peeling)

When an oxidized functionality, e.g., a keto or aldehyde group, is present along the cellulose chain, the β -elimination reaction can start by nucleophilic attack of a hydroxyl ion at this position, and the C-1 or C-4 substituent in the β -position is consequently eliminated (Fengel & Wegener 1984).

In the case of a C-6 aldehyde being present, a glycosidic cleavage occurs at the C-4, producing a novel reducing end group at the eliminated chain end and a rather stable fragment with a conjugated double bond. The C-4 substituent will also be eliminated when a C-2 keto carbonyl group exists. This reaction will also produce the eliminated unit with a new reducing end and an unstable enol-enone fragment, which undergoes a benzilic acid rearrangement transformation to an acid (Lai 2001). The β -elimination reaction of a C-3 carbonyl group will eliminate the C-1 substituent with a nonreducing end and eventually leave an acid after rearrangement. The keto group at C-2 and C-3 is interchangeable due to a keto-enol tautomerization under alkaline conditions (Potthast et al. 2006). C-6 and C-2 carbonyls are regarded as “active” carbonyls, since they lead to formation of a new reducing end group via β -elimination, which can trigger the peeling reaction consecutively, while a C-3 carbonyl is a “nonactive” carbonyl, producing a nonreducing end (Lewin 1997).

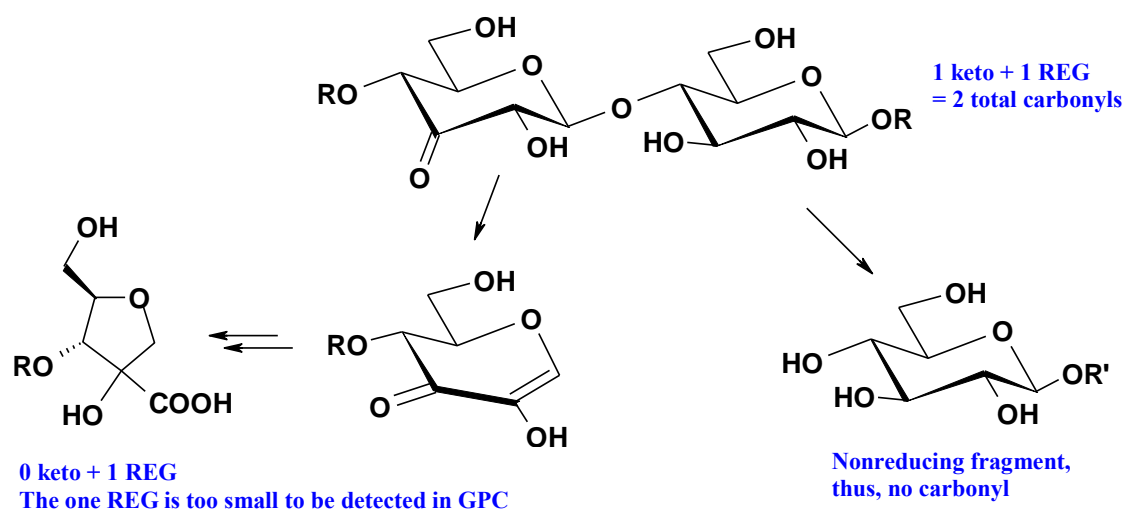


Fig. 1-2. β -elimination triggered by a C-3 carbonyl at the reducing chain end. The molecule starts with two carbonyl groups, including a REG, but no carbonyl will be detectable after reaction. No significant Mw loss accompanies the reaction, since only a short chain fragment is eliminated. (R = cellulose with a few DP and a reducing end; R' = a long cellulose chain with a nonreducing end)

This type of β -elimination reaction will cause glycosidic bond cleavage in the middle of the chain if a carbonyl group is present, resulting in severe fragmentation, unlike the endwise peeling reaction. In addition to lowering molar mass, it will yield a change in carbonyl groups, depending on where the original oxidation is present.

Influence of the oxidative β -elimination on molecular weight and the number of the total carbonyl groups is shown as Table 3 in Paper III. The number of carbonyl groups will decrease or remain the same after β -elimination, unless only C-6 carbonyls located in the middle of the cellulose chain trigger β -elimination selectively. The extent of the decrease is strongly affected by where the keto/aldehyde group is located along the cellulose chain. A significant decrease in the molecular weight is mainly accompanied by either a small loss or even an increase in carbonyl groups, while a stable value of the molecular weight always leads to a decrease in the carbonyl groups.

If a keto/aldehyde group is located at an AGU at the end of a cellulose chain, the β -elimination will not affect molecular weight significantly, since only one or very few AGUs are cleaved off. In this case, decrease of carbonyl groups is still visible. For example, the β -elimination reaction initiated by C-3 keto located in reducing chain ends is illustrated in Fig. 1-2, showing a decrease in the number of carbonyl groups and no

significant molecular weight change.

This type of β -elimination is important with respect to deacidification, as it can proceed at ambient temperatures and under mild alkaline conditions such as pH 9 (Potthast et al. 2006).

Model studies on oxidized model pulp or paper have demonstrated the possibility that cellulose degradation may occur after a deacidification treatment (Kolar & Novak 1996; Bogaard & Whitmore 2001; Malesič et al. 2002; Stephens et al. 2009). Generally, a higher carbonyl group content as well as a higher pH was found to yield a larger risk, which led to the recommendation of relatively low quantities of alkaline reserve to be deposited after mass deacidification.

1.4.3. Alkaline cleavage

A mechanism of scission of the β -D-glycosidic linkage at alkaline conditions, so-called alkaline hydrolysis, has also been proposed. It involves ionization of a C-2 hydroxyl group and change of the chair conformation, a process with a high activation energy. In subsequent steps, an oxiran ring is formed, eliminating an alkoxy group. This 1,2-anhydride may undergo hydrolysis, forming a reducing end group or a 1,6-anhydroderivative, i.e., levoglucosan (Lai 2001; Sjöström 1981).

As alkaline cleavage can occur in the middle of a cellulose chain, its impact on the molecular weight will be significant. However, it was found that the cleavage is extremely slow and needs much higher temperatures due to the high activation energy mentioned above, compared to the peeling reaction: 36–38 kcal/mol vs. 21.2–24.5 kcal/mol (Lai 2001, p. 475;). It becomes pronounced when the temperature rises higher than 170 °C (Fengel & Wegener 1984). Hence, a mass deacidification treatment hardly causes direct alkaline cleavage of cellulose.

1.4.4. Oxidation reactions

Cellulose under alkaline conditions may also undergo oxidative modifications. A prominent example is the so-called “Autoxidation.” From the chemical-mechanistic viewpoint, this is a free radical chain process, which can be typically divided into three steps of reactions: first, free radical formation by initiation reactions, secondly,

propagation reactions, and finally, the chain reactions terminated by e.g., recombination of two radical species. In cellulose chemistry, autoxidation is often discussed for oxygen bleaching (pH ~11) and for steeping and ripening of cellulose in the viscose process. Entwistle et al. (1949) proposed a radical mechanism to occur during the aging of alkali cellulose, which generally contains 15–18% NaOH. They elaborated oxygen pressure and metal ions as the main factors that may increase the reaction rate. For an effective delignification, alkali concentration and (elevated) temperature are major factors to promote the initiation step by ionization of the substrate and the reduction of molecular oxygen to reactive species such as hydroperoxyl and hydroxyl radicals (Schwanninger 2006). Polysaccharides may undergo chain scission by this mechanism when hydroxyl radicals are formed in the presence of heavy metals, e.g., by a Fenton-type reaction, and then may further oxidize cellulose as shown in Fig. 1-3 (Gierer 1997, as cited by Schwanninger 2006). According to the proposed reaction, hydroxyl radicals will lead to formation of carbonyl groups at C-2 in cellulose, which are in turn “hot spots” for β -elimination, that is, oxidative peeling reaction (see 1.4.2), under alkaline conditions (Fengel & Wegener 1984; Kolar 1997; Lai 2001).

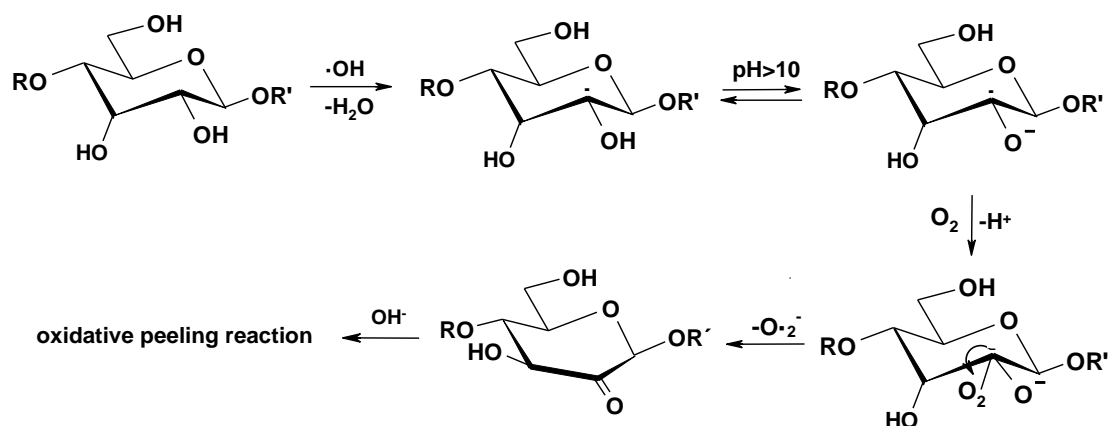


Fig. 1-3. Autoxidative degradation of cellulose under alkaline conditions proposed by Gierer (1997).

In paper conservation, paper containing mainly iron ink or copper pigment is considered to be more susceptible to autoxidative degradation. This led to the development of treatments with antioxidants as radical scavengers (Kolar et al. 2003; Malesič et al. 2005a, 2005b). In book paper, transition metal ions can also be present, e.g., 4–77 ppm of Cu in machine-made papers (Praskievicz & Subt, as quoted by Williams et

al. 1977). The copper ions are also very effective in catalyzing autoxidative degradation of cellulose. Lignin can be readily activated under alkaline conditions due to its phenolic units and can initiate radical chain reactions in the presence of oxygen (Ericsson et al. 1971). Whether lignin reacts as radical initiator or as antioxidant, simply by generation of stable radicals, highly depends on the conditions and on the lignin structure. In the first case, this may lead to degradation of carbohydrates (Guay et al. 2000; Guay et al. 2001). A slight increase in atmospheric oxidation of cellulose after deacidification was found (Arney et al. 1979), and formation of hydroxyl radical in the deacidified model papers during accelerated aging was confirmed (Kolar et al. 2001). However, autoxidative degradation of cellulose and the action of hydroxyl radicals are far from being completely understood, especially when it comes to aspects of natural aging of deacidified paper.

1.5. Criteria for evaluation of paper after mass deacidification

The pH and alkaline reserve of paper are primarily assessed after mass deacidification, as they must change if the treatment is carried out successfully. Visual inspection of bleeding of color or ink, discoloration of paper, or any alteration of the binding material can be followed by simple visual inspection or by a colorimetric instrument for evaluation of side effects of mass deacidification. As such optical and haptic criteria vary and are difficult to judge objectively, they can be evaluated by a Total Risk Indicator (TRI), which combines three factors—significance, frequency, and extent—as well as various corresponding criteria (Banik et al. 2006). A long-term effect of the treatment, which often involves an accelerated aging step, is generally investigated by measuring the degree of polymerization of cellulose and/or the mechanical properties of paper such as folding endurance or tensile strength. Copper number and (hot) alkali solubility are used to judge oxidative effect. Low molecular weight carbohydrates in paper were measured to obtain additional information on degradation of cellulose in some cases (Whitmore 1994; Lienardy 1994; McCrady 1991). Besides this, odor or toxicity can be a category to assess effects for the reader or end user.

The current DIN recommendations suggest the use of test papers for quality control of mass deacidification (Hofmann & Wiesner 2011). The specifications of the test papers are

shown in Table 1. Major providers of mass deacidification in Germany often present their data based on the measurements of these test papers.

Table 1 Specifications of test papers for quality standards (Klug-Conservation 2013a & 2013b)

	NOVO test paper 1 (lignin-containing paper)	NOVO test paper 2 (lignin-free paper)
Grammage	90 g/m ²	70 g/m ²
Pulp	> 55 % mechanical wood pulp (CTMP)	100 % bleached chemical
Composition	(lignin 17%) + bleached paper pulp	pulp
Filler	approx. 12–15 % kaolin	approx. 12–15 % kaolin
pH [*]	4.0–5.0 (adjustment with alum)	approx. 4.5 (same)
Sizing ^{**}	Cobb ₆₀ OS 19 / SS 21 g/m ²	Cobb ₆₀ OS 20 / SS 22 g/m ²
Type	Rosin and alum	Rosin and alum
Others for both	70 x 100 cm of size, no surface sizing, calendering, no optical brighteners	

* measured in the headbox

** water absorptiveness measured in 60 seconds according to TAPPI 441 om-98 (TAPPI 2004e)

The criteria for the evaluation of mass deacidification in this study were based on the quality standards of criteria currently available (Table 2): pH using the surface pH measurement (TAPPI 529 om-99 (TAPPI 2004a)), alkaline reserve by titration (ISO 10716: 1994 (ISO 2003a)) and elemental analysis using XRF verified in accordance with SN EN 45001 (Blüher & Vogelsanger 2001, p 985), and examination of the distribution of alkaline reserve by SEM-EDX. In addition, cellulose analysis was applied using GPC with fluorescence labeling of oxidative functionalities of cellulose.

Table 2 Currently recommended quality standards for mass deacidification *

	DIN recommendation (Hofmann & Wiesner 2011)	Internal standards of the Papersave Swiss TM process (NCW 2004)	Requirements from the Library of Congress (n.d.b)
pH	test paper ≥ 7 (surface and/or cold)	98% of tested paper ≥ 7 (surface and/or cold)	6.8–10.4
Alkaline reserve (%w/wMgCO ₃)	test paper 0.5-2.0% (titration)	95% of test paper 0.5–2.0% ^{**} 95% of original paper 0.3–2.3% (XRF)	1.0–3.0% ^{***}
Homogeneity of alkaline reserve	not specified, (ICP-OES)	95% of tested paper SD ≤ 0.5 (XRF)	not specified
Long-term effect after accelerated aging	not specified, (tensile strength)	not specified	300% increase (folding endurance)

*Parenthesis indicates the determination method if available

**Uptake of alkali

*** Alkaline substance not specified

1.5.1. pH

The pH of paper determines a concentration of hydronium ions extracted from paper in water rather than actual acidity or alkalinity of paper, which is neutralizing capacity (Banik 2011). Accurate measurement of pH by current extraction methods can be influenced by other components soluble in water that may interact with hydronium ions in water. The ratio of the amount of paper and water depends on the standard method, and the extraction method also varies (TAPPI 509 om-02 (TAPPI 2004b); TAPPI 435 om-02 (TAPPI 2004c); ISO 6588-1 (ISO 2006a); ISO 6588-2 (ISO 2006b)).

When surface pH measurement using a flat electrode is carried out for paper, more cautions are required; surface characteristics such as coating and sizing agents and the density of paper will influence the absorbency and penetration of water, leading to a relatively larger variation of the pH. A flat electrode in direct contact with the paper surface may mislead the electric potential of the electrode due to the charged fibers and particles on the paper surface (Strlič et al. 2004). Empirical studies showed that the surface pH tended to be lower than the pH of the paper determined by the cold extraction

method (Saverwyns et al. 2002; Bansa & Hofer 1984; Strlič et al. 2004; Blüher 2006). The low solubility of alkaline earth carbonates should be considered in addition to the systematic error of the surface pH measurement method explained above and the influence of CO₂ in the atmosphere (Kelly 1989; Strlič et al. 2004). Consequently, in case of the Papersave SwissTM process, surface pH between 5 and 7 after mass deacidification is still regarded as “completion” of the treatment as long as another alternative method proves the tested item is no longer acidic (NCW 2004).

Despite the disadvantages of the surface pH measurement, it is often used as an assessment tool of mass deacidification of books and archival material. This is because it is relatively easy and fast and much less laborious compared to other extraction methods. It can be cost-effectively applied in-house in libraries and archives with little man power. More importantly, as it requires no sampling, although it might cause water stains, it can be applied directly to original materials after mass deacidification.

A standardized method published by TAPPI (TAPPI 529 om-99 (TAPPI 2004a)) is available to assist surface pH measurement of paper. However, relatively poor reproducibility has been observed even within the same lab due to lack of details in the standard method, e.g. the definition of “a drop of water,” the duration of measurement, and allowable drift range for the final reading. In order to reduce fluctuations induced by the measurement procedure, a more detailed protocol should be established to improve accuracy and reproducibility.

1.5.2. Alkaline reserve

In addition to the neutralization of existing acid, depositing of alkaline compounds is an important aspect of mass deacidification. The role of alkaline reserve for long-term paper stability was mentioned already in the 1930s (Hanson 1939); historic rag papers in good condition contained at least 2% of calcium carbonate. Various international and national standards for paper permanence also require 2% of calcium carbonate as a minimum amount of alkaline reserve (ISO 9706: 1994 (ISO 2003b), ISO 11108: 1996 (ISO 2003c), ANSI Z39.48: 1992 (ANSI 2002), and DIN 6738:2007-0 (DIN 2007)). Compared to the standards for paper permanence, the requirement for alkaline reserve after mass deacidification is relatively moderate, taking into account the risk of alkaline degradation of oxidized cellulose (see Table 2).

The unit, mol/kg, can be used if no particular alkali substance is specified. When available, weight percentage of the alkali compound per weight of paper (% w/w) is often used. Current available standards or recommendations indicate the standard for alkaline reserve on the assumption that alkaline reserve is present as MgCO_3 . However, the transformation of alkaline reserve during the evaporation of solvent and the reconditioning step has not been investigated in detail. Blüher and Vogelsanger (2001) assume that the final alkaline reserve may be in a mixture of MgCO_3 , $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$, and $\text{Mg}(\text{OH})_2$ after applying the Papersave SwissTM process. In case of the BookkeeperTM process, transformation of MgO to $\text{Mg}(\text{OH})_2$ is confirmed at 80% RH (Polovka et al. 2006). The final form(s) of alkaline reserve after major nonaqueous deacidification processes could be, rather, in a form(s) of basic magnesium carbonates, because magnesium hydroxide tends to coprecipitate in the form of basic magnesium carbonate under the condition of atmospheric carbon dioxide (Smith 2011). Defining which alkaline compound(s) is formed and how it transforms to another species is important, since it is related to pH and alkaline degradation induced by high pH as well as to the efficacy of neutralization with acids (Whitmore 1994).

Alkaline reserve by titration

For the wet-chemical determination of alkaline reserve, the standardized methods are available (TAPPI 553 om-92 (TAPPI 2004d), ISO 10716:1994 (ISO 2003a)). Both standards require 1 g for the titration of alkaline reserve and 2 g for determination of moisture content and employ acid-base back-titration to ensure complete extraction of alkali. Basically, the extraction of alkali compounds is carried out by adding a sufficient amount of acid (0.1N HCl), assisted by heat. The excess amount of acid is titrated back with 0.1N NaOH. Since naturally aged paper pieces are generally discolored, and some of the chromophores are soluble in water, the end point is not easy to determine by a color indicator like methyl red (2-(4-Dimethylaminophenylazo)benzoic acid), as recommended by both standard methods. To overcome this problem, the pH change during titration can be followed in addition by a pH electrode. Often problematic is the fact that several equivalent points can be found, depending on the paper types and the concentration of alkali (Bukovsky 2005); hence, they are difficult to detect precisely when measurements are manually conducted. In this case, finding an end point at pH 7 is

generally pursued (Kelly 1989).

Determination of the homogeneity of alkaline reserve within a paper sheet using the titration methods is not practically possible, as the 1 g of required sample amount can be half a page or an entire page, depending on the size of book. Besides, these methods are time-consuming and laborious, leading to difficulty of application to a larger number of samples. Therefore, the development of faster and more nondestructive or minimally invasive methods is urgently required.

Alkaline reserve and its homogeneity by XRF

X-ray fluorescence spectrometry (XRF) is one of the most widely used analytical techniques in the field of art conservation. It offers nondestructive elemental analysis of art objects using the characteristic X-ray fluorescence of each element in the sample excited by an incident X-ray beam. When it is applied to quantitative analysis, however, several factors need to be concerned: mass absorption coefficients of all elements in the sample and enhancement effects due to a secondary excitation in addition to excitation by an incident beam (Skoog & Leary 1992). Therefore, calibration with external and/or internal standards that possess a similar matrix to the sample is generally required. In situ XRF analysis of thin objects can resolve the matrix effects somewhat (Markowicz 2011). However, paper is heterogeneous and varies in terms of such things as thickness, density, and physical and chemical composition (Barrett et al. 2012). Moreover, Mg—the element of interest in major mass deacidification processes—can be detected only from the superficial surface of paper due to its low atomic mass, i.e. its low emission energy.

Despite its instrumental disadvantages with regard to quantitative analysis, NCW AG, Switzerland, developed a method for the determination of alkaline reserve by means of XRF and has been actively applying this method within quality control of the Papersave SwissTM process. Having a constant ratio of Ti to Mg in the treated paper allows the assessment of the Mg content via Ti by XRF (Blüher & Vogelsanger 2001; Andres et al. 2008). Thus, Ti is measured and the relative amount of Mg and % MgCO₃ calculated. Several assumptions are made:

- The uptake ratio of Ti and Mg is always assumed constant for any original material;
- The acid content of original materials is set equal to -0.3% of MgCO₃;

- Ti is not originally present in the original materials prior to deacidification (Andres et al. 2008).

Although it is a fast and nondestructive method for determination of alkaline reserve, a major disadvantage of this method is that only paper treated by the Papersave™ process or the Papersave™ Swiss process, which uses a complex of magnesium-titanium ethoxide as the active agent, can be analyzed.

NCW utilizes XRF also for the determination of homogeneity of alkaline reserve within a single paper sheet, as it requires only 150 mm² of measuring area (Blüher & Vogelsanger 2001). If more than 95% of the tested books meet the standard deviation (> 0.5 on 6–7 measurements per page), the deacidification is regarded as a “homogeneous” treatment (Blüher 2006; Reist 2006; Andres et al. 2008).

Alkaline reserve and its homogeneity using ICP

ICP (Inductively Coupled Plasma), a common method in elemental and isotope analysis, can be applied for the determination of alkaline reserve. ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) ionizes or atomizes the nebulized sample solution by hot plasma and detects radiation at the characteristic wavelengths of the target ions. In order to analyze the alkaline reserve such as MgCO₃ in paper by ICP-OES, the sample paper should be digested by acid(s); hence, it requires destructive sampling. As only a few hundred milligrams of paper are used per measurement, ICP-OES can be applied for the determination of homogeneity within a single paper sheet. Like any other elemental analyses, it measures the uptake of alkali, not alkaline reserve, based on the assumption that all detected magnesium is from alkaline magnesium compounds and that no magnesium is present before mass deacidification unless a non-deacidified duplicate paper is also analyzed.

ICP assisted by laser ablation (LA-ICP) does not require sample preparation, since laser fragments and vaporizes a solid sample directly. When it is coupled with a mass spectrometer (MS), precision and detection limits improve compared to ICP-OES.

Distribution of alkaline reserve on the surface and in the paper matrix by SEM-EDX

While a centimeter resolution of homogeneity of alkaline reserve is possible with

XRF or ICP-OES, micron to millimeter scale of examination can be carried out with scanning electron microscopy in combination with energy dispersive X-ray analysis (SEM-EDX or SEM-EDS). A high resolution of imaging of the sample surface can be accomplished by detecting secondary or backscattered electrons emitted from a specimen and then amplifying the electrical signal generated. When an X-ray detector is also installed, the characteristic X-ray emission from each constituent atom of sample can be identified. Therefore, with SEM-EDX, not only visualization of alkaline reserve particles is possible, but the identification of alkaline reserves can also be carried out. In addition, any changes in surface properties, such as coating or sizing and damage of fibers after deacidification, can be defined. Appropriate sample preparation techniques allow a cross-sectioned area of paper also to be analyzed, which is important in judging the distribution of alkaline reserve into the paper matrix.

SEM-EDX can identify which alkaline reserves are formed if they have characteristic crystal structures. Otherwise, it again measures uptake of alkali, e.g., both magnesium sulfate and magnesium carbonate. Since the analytical results of SEM-EDX are generated from a fine local area, an effort to acquire representative data and images of the sample should be made, as mentioned by McCrady (1987). A small size of sampling from the original paper is inevitable.

1.5.3. Cellulose analysis by GPC

Gel permeation chromatography (GPC) is one of the important analytical tools for polymer characterization. Separation of polymeric molecules according to their hydrodynamic volumes allows defining of the molecular weight (MW) and molecular weight distribution (MWD). It can be used for investigation of the polymerization mechanism or condition as well as the degradation state (Mori & Barth 1999a, p.1). Cellulose, a natural linear homopolymer, has also been studied using GPC to monitor its molecular structure. In the field of conservation of paper, early literature about the characterization of paper using GPC can be found in the 1980s (Burgess 1982). When mass deacidification processes were actively developed and applied to library books in the 1990s, however, evaluation of the processes mostly depended on mechanical properties of paper for a long-term effect of deacidification. Folding endurance or strength tests of paper can provide information on the durability of paper rather than on

permanence. When deterioration of paper is observed, it indicates that chemical changes in cellulose occur (Hendriks 1994). In other words, knowing the mechanical properties of paper without knowing the chemical properties of cellulose is not enough to discuss the long-term survival of paper or what is really occurring in paper, since mechanical properties are secondary parameters that result from chemical changes. Besides, mechanical tests of paper require a large amount of sample to acquire reasonable data that can be representative of heterogeneous samples like paper. When a GPC is coupled not only with an RI detector but also with detectors such as MALLS, UV, or fluorescence, it becomes a more sensitive and powerful tool for cellulose analysis. Chemical fluorescence labeling techniques of oxidative functionalities of cellulose allow us a deeper insight into oxidation states in relation to the molecular weight distribution (Röhring et al. 2002a, 2002b; Potthast et al. 2003; Bohrn et al. 2006; Potthast et al. 2006). These techniques are especially valuable in paper conservation, since oxidative functionalities of cellulose are important factors in investigating degradation mechanisms. The sample requirement being on the milligram scale can be considered an additional advantage of this method. In the following paragraph, the data that can be obtained from cellulose GPC analysis are explained in more detail, and applications are discussed.

Molecular weight of cellulose

Molecular weight-related values that can be produced by GPC are usually the weight-average molecular weight (M_w), the number-average molecular weight (M_n), and the z-average molecular weight (M_z). The definitions of these values are given in the following: M_w is the sum of the square of each molecule's weight divided by the total weight of all molecules; M_n is the total weight of all molecules divided by the number of molecules. Therefore, M_n is the typical arithmetic average of molecular weights of all molecules, while M_w is a weighted average. M_n is more sensitive to smaller molecules present in the distribution. M_z is sometimes called size average molecular weight, and it depends on heavy (large) molecules more than M_w or M_n , as seen in Fig. 1-4.

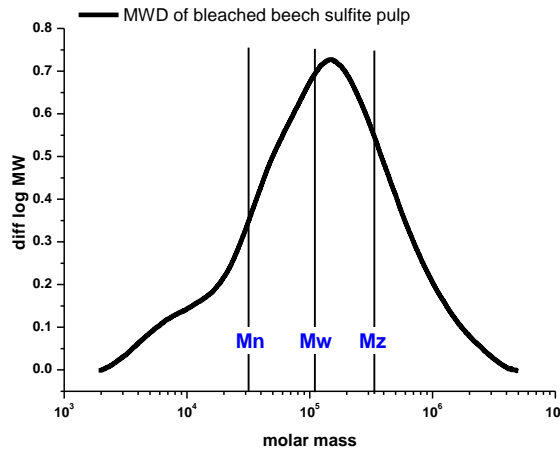


Fig. 1-4. MWD of a bleached sulfite pulp with values for Mw, Mn, and Mz.

For actual calculation of molecular weight averages from a GPC chromatogram, the retention volume of the i^{th} point (V_i), the height of the chromatogram at the i^{th} point (H_i), and the molecular weight from the calibration curve at the i^{th} point (M_i) are produced and processed with the following equations (Mori & Barth 1999b, p 80).

$$M_n = \frac{\sum H_i}{\sum (H_i/M_i)} \quad (1)$$

$$M_w = \frac{\sum H_i M_i}{\sum H_i} \quad (2)$$

$$M_z = \frac{\sum (H_i M_i^2)}{\sum (H_i M_i)} \quad (3)$$

When a MALLS detector is connected to GPC, no more calibration with known polymers similar in structure to the unknown sample is necessary. The light scattering detector allows us to determine the weight-average molecular weight directly. In addition, the radius of gyration of a polymer can be measured. An important equation for determination of these parameters is the ZIMM equation (equation (4), Wyatt 1993):

$$\frac{K^* c}{R(\theta)} = \frac{1}{M_w P(\theta)} + 2A_2 c \quad (4)$$

where K^* is the optical constant, c is the concentration of cellulose in the solution, $R(\theta)$ is the excess Rayleigh ratio of the solution, θ is the scattering angle, $P(\theta)$ is the angular dependence of the scattered light which is related to the RMS radius, and A_2 is the second virial coefficients, respectively. The constant, K^* , is defined by equation (5):

$$K^* = \frac{4\pi^2 n_o^2 \left(\frac{dn}{dc} \right)^2}{N_A \lambda_o^4} \quad (5)$$

where N_A is Avogadro's number, n_o is the refractive index of the solvent used, λ_o is the wavelength of the incident light, and dn/dc is the change of the solution's refractive index with the change of molecular concentration, which is dependent on the polarizability of a solution of cellulose.

Actual estimation of Mw can be accomplished by the Zimm plot, as shown in Fig. 1-5 (K' is an arbitrary constant). In this plot, the inverse of Mw can be obtained by extrapolating the lines to zero concentration and to a scattering angle of 0° (Mori & Barth 1999c).

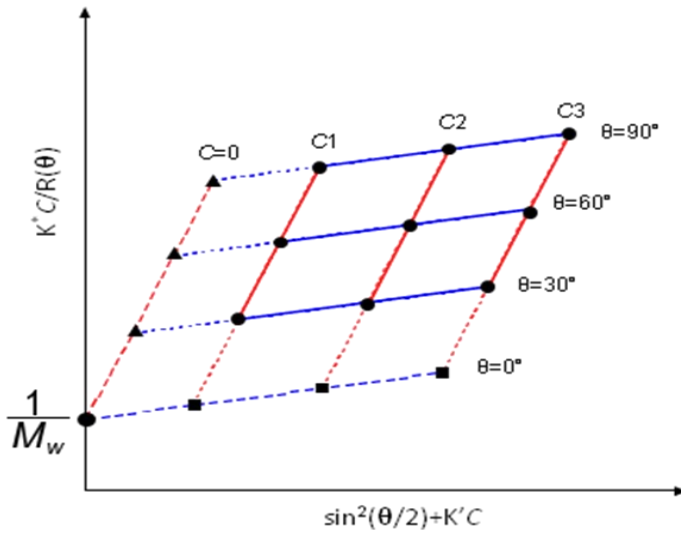


Fig. 1-5. Zimm plot assisting determination of Mw by two extrapolations to 0° angle and zero concentration (Mori & Barth 1999c, p. 116).

Therefore, separated cellulose molecules can be characterized online in GPC using a light scattering detector. Instead of column calibration or universal calibration with

known polymers, the GPC-MALLS system requires only a basic preadjustment of the MALLS detector with a pure solvent and normalization with an isotropic scatterer, e.g., small Mw polystyrene, prior to the actual analysis of cellulose (Podzimek 2011).

From the obtained Mw (g/mol), the degree of polymerization (DPw) of cellulose can be calculated by dividing by the molar mass of an AGU unit, ~162 g. When hydrolytic degradation rates of cellulose are considered, the well-known Ekenstam equation can be applied using calculated DPw. The rate constant of hydrolysis, k , at a given temperature, can be calculated by a simplified zero-order kinetics (Ekenstam et al. 1936, as cited by Sixta 2006; Zou et al. 1996):

$$\frac{1}{DP_t} - \frac{1}{DP_0} = kt \quad (6)$$

where DP_t is average degree of polymerization after time t , DP_0 is its initial value at $t=0$, and k is the rate constant of hydrolysis, which indicates the number of broken bond per AGU.

Whereas the Ekenstam equation tells the number of broken bonds, its modified equation, $S=617 (1/DP_t - 1/DP_0)$, is subjected in order to define the chain scissions in mmol per 100 g of cellulose, so that it can be readily compared to contents of oxidative functionalities in the same unit (Whitmore & Bogaard 1994; Calvini 2012).

While the Ekenstam equation is widely used without question, the expanded Ekenstam equation has also been proposed compensated by leveling-off degree of polymerization (LODP), taking into account the degradation of the crystalline region in cellulose (Calvini 2005; Calvini 2012).

$$\left(\frac{1}{DP_t} - \frac{1}{DP_0} \right) = \left(\frac{1}{LODP} - \frac{1}{DP_0} \right) \times kt \quad (7)$$

Once k values are determined at different temperatures (T), the rate constant at room temperature can be defined by extrapolation, using the “Arrhenius plot,” which generally illustrates $\ln k$ vs. $1/T$ according to the following equation:

$$\text{Arrhenius equation } k = Ae^{(-E_a/RT)} \quad (8)$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant.

Recently, a new degradation equation of cellulose has been presented. It is based on percentage DP loss or percentage loss of tensile strength as shown in the following equation (Ding & Wang 2008a, 2008b):

$$\omega_{DP} \equiv 1 - \frac{DP_t}{DP_0} = \omega_{DP}^* (1 - e^{-kDP_t}) \quad (9)$$

where ω_{DP} is the degree of degradation and ω_{DP}^* is the capacity of DP degradation reservoir. The authors claimed that a new kinetic model can characterize degradation of different cellulosic materials under various accelerated aging conditions. The equation explains the chain scission activity of cellulose better and can be universally applied to chain scissions brought about by different degradation mechanisms.

Molecular weight distribution and PDI

In order to measure the molecular weight distribution of polymers in solution, an appropriate method for MW detection has to be applied. A MALLS detector is applied together with refractive index (RI) detector, which is concentration sensitive, eventually leading to a reliable determination of MWD.

The molecular weight distribution (MWD) is valuable information for the structure of cellulose. The polydispersity index (PDI) represents the width of a MWD and is easily calculated by the following equation when Mw and Mn are available:

$$PDI = \frac{M_w}{M_n} \quad (10)$$

A lower PDI indicates a narrower MWD and vice versa.

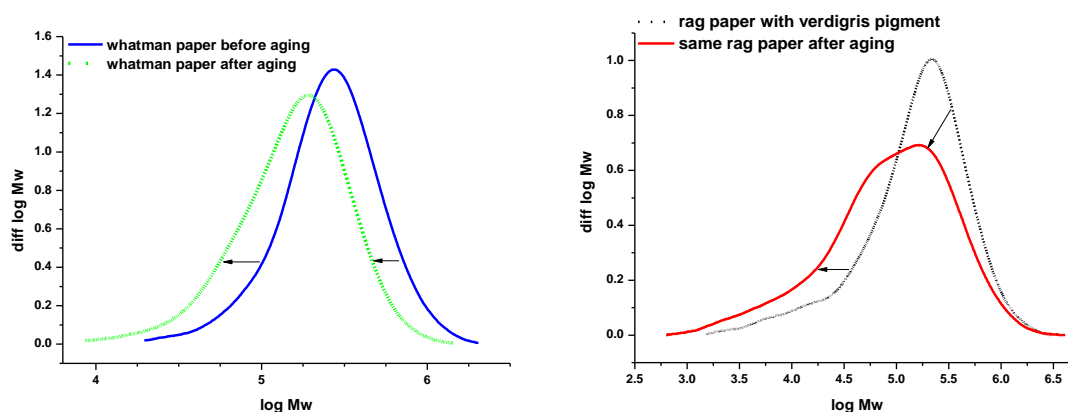


Fig. 1-6. Different degradation patterns can be found in MWD of different papers after accelerated aging. Left: MWD of Whatman papers before and after accelerated aging under dynamic conditions of temperature and humidity. Right: MWD of rag papers with verdigris pigment before and after accelerated aging at 80 °C and 65% of RH.

For example, Whatman paper containing almost pure alpha-cellulose, which is used often as a reference paper for an accelerated aging study, undergoes an overall MWD shift towards the lower molecular weight region, retaining PDI after artificial hot and humid aging. On the other hand, rag paper that suffered from copper-induced degradation due to the presence of verdigris pigment displays a larger shift of the short cellulose chains towards the lower molecular weight region and a distinct pattern in the high Mw area, leading to a bimodal distribution resulting in a wider MWD, i.e., higher PDI after the aging (Fig. 1-6). In case of kraft pulp, which generally exhibits a distinctive bimodal pattern of MWD due to the large amounts of hemicellulose present, MWD can even show changes in the cellulose and hemicelluloses ratio after applying various pulping or bleaching conditions (Sjöholm et al. 2000; Berggren et al. 2003).

Any change in MWD due to chemical treatment or aging can also be presented numerically, as seen in Fig. 1-7. Whereas the percentage portion of the high molecular weight region, $DP > 2000$, rapidly decreases during the aging, the molecular weight region, $DP < 2000$, relatively increases.

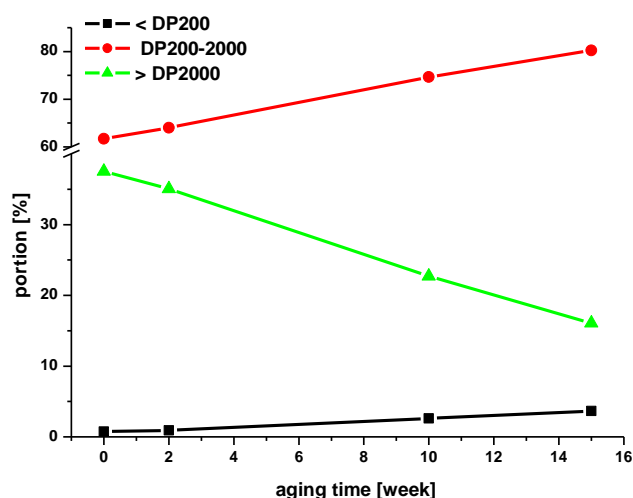


Fig. 1-7. Change of DP portion (%) of Whatman paper no. 1 during a dynamic accelerated aging.

Oxidative functionalities determined by fluorescence labeling

After chemical labeling of carbonyl groups with CCOA (Carbazole-9-Carbonyl-Oxy-Amine) and carboxyl groups with FDAM (Fluorenyldiazomethan) (Fig. 1-8), the respective oxidative functionalities can be detected and quantified in each fraction of the molar mass distribution by a fluorescence detector coupled to GPC. Therefore, in addition to quantification of the total content of carbonyl or carboxyl groups, it allows the collection of profiles of oxidative functionalities in relation to the molecular weight distribution.

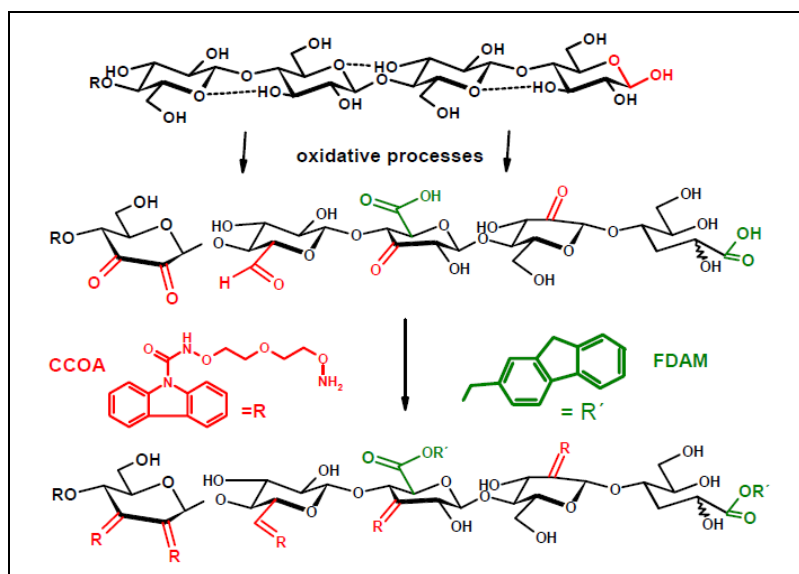


Fig. 1-8. Schematic overview of labeling of carbonyl and carboxyl groups of cellulose with selective fluorescence markers (Potthast & Henniges 2006, p. 113, Figure 2).

The oxidative functionalities can be given as a degree of substitution plot or in the form of pie charts that show their numerical amounts in a specific molecular weight region (Potthast & Henniges 2006). Overall, this leads to a deeper understanding of where exactly change in carbonyl groups or carboxyl groups occurs during cellulose aging or a chemical treatment. For example, copper ion-impregnated rag paper shows that more total carbonyl groups are introduced in the low molecular weight region after hot and humid accelerated aging (80 °C and 65% RH) (Fig. 1-9).

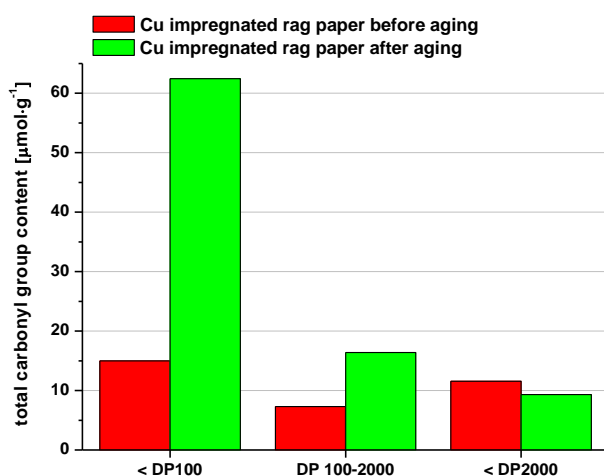


Fig. 1-9. Total carbonyl group contents of Cu ion-impregnated rag paper in the corresponding MW regions before and after accelerated aging.

From M_n determined by GPC, the average content of the reducing end groups can be calculated:

$$\text{REG}(\mu\text{mol} \cdot \text{g}^{-1}) = \frac{1}{M_n(\text{kg} \cdot \text{mol}^{-1})} \times 1000 \quad (11)$$

Thus, the along-chain carbonyl content, i.e., the keto/aldehyde carbonyl groups along the cellulose chain, can be determined and allow studying for a more detailed analysis of oxidative functionalities in cellulose (Potthast et al. 2008).

$$\begin{aligned} &\text{Along-chain carbonyl content } (\mu\text{mol} \cdot \text{g}^{-1}) \\ &= \text{Total carbonyl content } (\mu\text{mol} \cdot \text{g}^{-1}) - \text{REG content } (\mu\text{mol} \cdot \text{g}^{-1}) \end{aligned} \quad (12)$$

It should be noted that the content of along-chain carbonyl groups calculated by equation (12) may present a higher error range compared to the total carbonyl group content (about 3-4% RSD (Röhring et al. 2002b)). It is because the number of REGs is calculated from M_n , which has a higher RSD than M_w in GPC analysis and relies on the assumption that the reducing ends are not oxidized previously.

2. Materials and Methods

2.1. Surface pH (Paper I)

Fig. 2-1 presents a histogram showing the number of sample books analyzed for surface pH by year of deacidification and by the mass deacidification process applied. Measurement was performed at two different sites; the 282 books from the collection of the German National Library (DNB) were analyzed at the conservation department of the DNB in Leipzig, and the 161 books from the Berlin State Library (SBB) were measured at the Department of Chemistry of the University of Natural Resources and Life Sciences, Vienna (BOKU). An identical pH meter (Mettler Toledo SevenEasy™) and a flat combination pH electrode (Mettler Toledo InLab™ Surface, pH 1–11, 0–50°C) were used in both institutions.

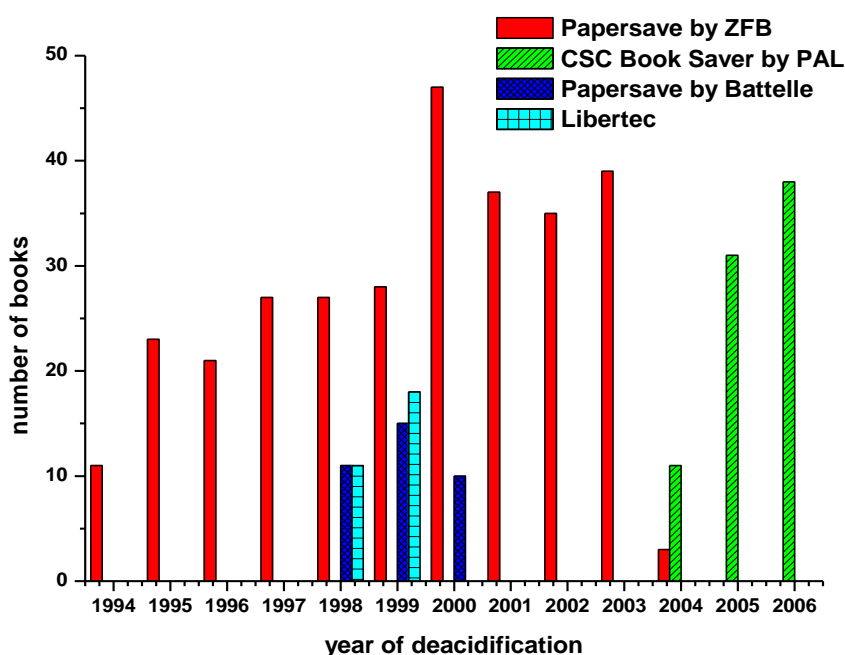


Fig. 2-1. Histogram of the sample books by year of deacidification and deacidification process.

Calibration of the pH electrode was obtained according to the TAPPI standard method, T529 om-99, using commercially available standard buffer solutions from Aldrich™. The measurements were performed with water of identical grade of purification, provided by

BOKU at both measuring sites. Two areas in the center and at the upper right margin of pages positioned in the middle of the book block were measured first. If the difference between the center and margin exceeded one pH unit, a second page from the middle of the book block was measured in addition. Therefore, all results presented here are averaged values of two or four measurements. Fifty-one selected books from the DNB were measured additionally at two areas at the beginning of the book block, to investigate homogeneity within a book.

Detailed protocols of the improved surface pH measurement method are given in Paper I.

2.2. Alkaline reserve (Paper I and II)

2.2.1. Titration

Twenty-two deacidified books were selected for investigation of the amounts of alkaline reserve deposited by mass deacidification. Additionally, seven non-deacidified duplicates were obtained from the antique markets in order to measure the acid content before deacidification. Sample books were published from 1892 to 1986 and were deacidified between 1994 and 2006. Ten books had been treated by the CSC Book SaverTM process operated by PAL, 11 books had been treated by the PapersaveTM process operated by ZFB, and one book had been deacidified by the LibertecTM process.

A description of the titration method is given in Paper I and II. Alkaline reserve calculated in mol/kg is converted into percentage (% w/w) of MgCO_3 on the assumption that all alkali compounds have been transformed to MgCO_3 .

2.2.2. Alkaline reserve determined by XRF

Twenty-eight books from the German National Library in Leipzig (DNB) and 12 books from the Berlin State Library (SBB) were analyzed using XRF. As explained in the introduction, only books treated with the PapersaveTM process could be included. Deacidification of four books was carried out by Battelle, and ZFB treated the rest. While books from the SBB were published from the 1840s to 1930s and deacidified from 1998 to 2003, books from the DNB were younger, published between the 1920s and 1990s and deacidified between 1994 and 2003.

The analysis was performed by NCW AG, Switzerland. Titanium contents on 6–7 spots of the middle page of each book were measured, and then the relative amount of Mg and % w/w of MgCO_3 was determined according to the uptake ratio of Ti and Mg and the calibration to the known amounts of % w/w of MgCO_3 , respectively. The average value of 6–7 spots will be given as the amount of alkaline reserve achieved by mass deacidification, and the standard deviation will address homogeneity of alkaline reserve within a single paper sheet. The conditions of XRF measurements are given in Paper II. The percentage (% w/w) of MgCO_3 determined by XRF analysis will be expressed as % MgCO_3 (XRF).

2.2.3. SEM-EDX examination of distribution of alkaline reserve

Three books treated by LibertecTM, PapersaveTM, and CSC Book SaverTM were selected to determine the alkaline reserve on the surface and within the paper matrix, using SEM-EDX. Duplicates of the three books were included as nontreated references. The following books were chosen:

- LibertecTM treated: published in 1913 and deacidified in 1998, 0.3% of MgCO_3 /surface pH 9.3;
- PapersaveTM treated: published in 1968 and treated in 1998, 1.2% of MgCO_3 /surface pH 8.4;
- CSC Book SaverTM treated: published in 1988 and treated in 2005, 0.7% of MgCO_3 /surface pH 8.8.

Au coating was applied to all samples for 60 seconds, and 30 kV of accelerating voltage was used on a Hitachi S-4000 device.

2.3. Cellulose analysis (Paper III and IV)

2.3.1. Sample papers and mass deacidification treatment

Twenty-five deacidified books were selected from the DNB in Leipzig and the SBB. Their duplicates were obtained from the antique markets in central Europe and analyzed together with the deacidified books. Therefore, a book “set” refers to a deacidified book and its non-deacidified duplicate. Three different mass deacidification processes were applied; one book was treated with the LibertecTM process, six books were treated with

the CSC Book Saver™ process, and 18 books were treated with the Papersave™ process. Whatman filter paper no. 1 served as the reference paper containing almost pure α -cellulose without sizing or fillers.

The list of sample books is shown in Table 1 in Paper III.

2.3.2. Accelerated aging

As paper is a complicated composite material, obtaining a representative sample from each book is essential for accelerated aging as well as for sample preparation for GPC analysis. Half a single paper sheet from the middle of the book block was cut as shown in Fig. 2-2, left, and applied to the accelerated aging for 15 weeks. Kinetic studies of aging under the accelerated aging conditions applied were carried out for eight book sets, aging for 14, 70, and 105 days after cutting two single paper sheets each, as shown in Fig. 2-2, right, in order to avoid inhomogeneities due to natural aging (Brandis & Lyall 1997) and deacidification. For these samples, three paper sheets were taken from the different sections of each book block.

A dynamic aging method in a closed system was chosen as an accelerated aging method. It offers relatively similar conditions to the natural aging of book paper, accumulating degradation products within the book (Bégin & Kaminska 2002; Shahani 1994). Having sample pieces from each book stacked to each other allows accumulation of degradation products between the stacks as in the situation of book paper. Finally, the stacks were sealed with several layers of aluminum foil. Accelerated aging conditions are given in Paper IV.

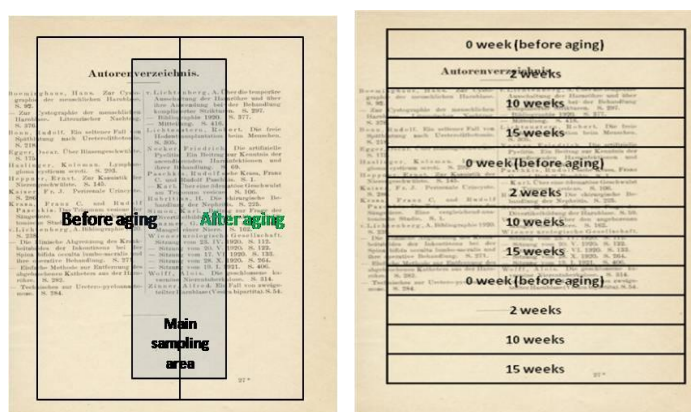


Fig. 2-2. Sample preparation for accelerated aging. Left: Books for application of one aging period (105 days). Right: Books for kinetic studies of aging (14, 70, and 105 days).

2.3.3. Impregnation of alkaline reserves into model book papers and their accelerated aging

Two book papers were selected and treated with various concentrations of magnesium propoxycarbonate deacidification reagent (CSC Book SaverTM by Conservacion de Sustratos Celulosicos S.L., Spain) to create different amounts of alkaline reserve in the papers. Solutions of 5, 10, 20, and 40% (v/v) in 1-propanol were sprayed on the front and the back of each book paper. Excess solution was removed by placing them between blotting papers. Samples were dried and stored under ambient conditions until artificial aging started. Whatman paper no. 1, as a reference, was also treated in a same way, together with the model book papers. The samples were aged in a chamber at 80 °C and 65% relative humidity for approximately 43 days (1029 h), according to ISO 5630-3:1996 (ISO 2003d). Samples were not completely sealed, but were still stacked to simulate a book during accelerated aging. The accelerated aging conditions were not exactly identical to the conditions applied to the original book samples. However, Whatman paper confirmed comparable degradation mechanisms to the dynamic accelerated aging method applied to the original book samples.

2.3.4. Exposure to acetic acid vapor

The exposure was performed in a closed desiccator for four weeks at ambient temperature. All the samples, the deacidified papers and their non-deacidified duplicates, were exposed together to 400 mg/m³ using acetic acid in a saturated NaCl solution, which maintained RH at around 75%. Weight of sample was measured after continuous off-gasing for one week.

2.3.5. Sample preparation for GPC analysis

CCOA (Carbazole-9-Carbonyl-Oxy-Amine) labeling of carbonyl groups was performed as described in the literature (Röhring et al. 2002a, 2002b; Potthast et al. 2003).

In order to analyze a sample that represents a large area of paper, about 100 mg were taken from each sample book and disintegrated in a mixer with demineralized water. After filtering off the water, 25 mg of wet fibers was collected in a 4 ml vial and labeled

with CCOA dissolved in 0.02M zinc acetate buffer solution (1.25 g/L) at pH 4.0 for 7 days at 40 ° C. After the labeling reaction, excess CCOA was filtered, and the collected fibers were washed thoroughly with water and also with ethanol. After solvent exchange in DMAc overnight, excess DMAc was removed, and then the paper fiber was finally dissolved in 1 ml of DMAc/LiCl 9% (w/v) for one or two days, depending on the dissolution state of samples. For GPC measurement, it was diluted with DMAc (1:3) and filtered with 0.45 μm PTFE filter. Simplified procedures of the sample preparation for GPC analysis are illustrated in Fig. 2-3.

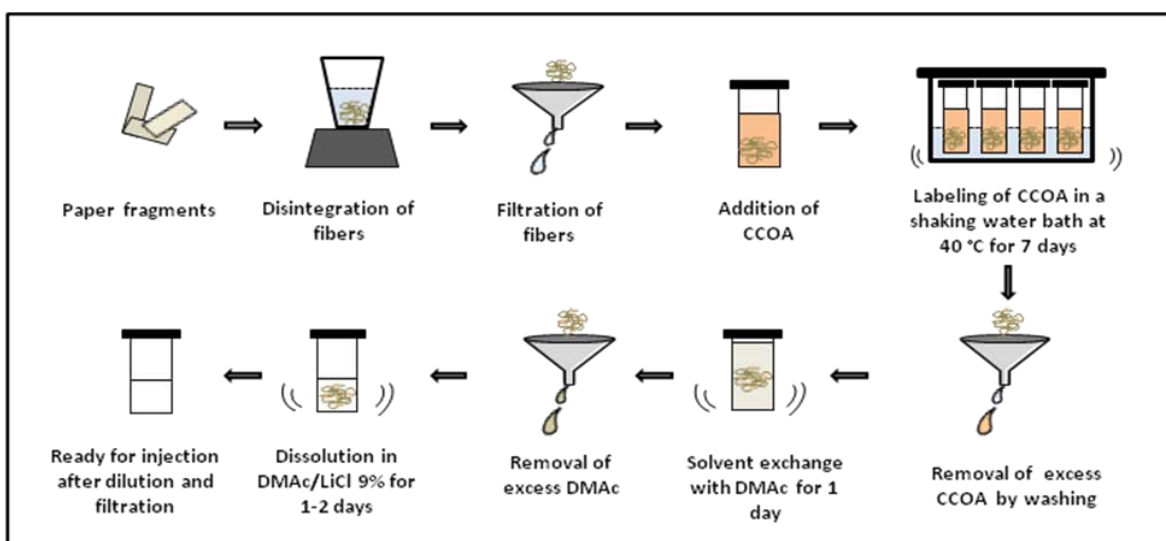


Fig. 2-3. Simplified scheme for sample preparation for CCOA labeling and GPC analysis.

GPC conditions and data processing were as written in Paper III and IV.

3. Results and Discussion

3.1. Present conditions of the books deacidified from 1994 to 2006—Surface pH & alkaline reserve (Paper I & II)

3.1.1. Data overview

Four hundred and forty-three books from the DNB and the SBB had a pH mainly between 6.5 and 9.5, according to the surface pH measured in 2009 and independent of the year of deacidification (Fig. 6a & 6b in Paper I). Eighty percent of the books showed a pH higher or equal to pH 7. Considering that a neutral pH is used commonly as a minimum target value for mass deacidification (Hofmann & Wiesner 2011; NCW 2004), the quality of the mass deacidification processes applied to these two libraries from 1994 to 2006 needs to be improved.

Results from alkaline reserve measurements shared a similar trend. Twenty-one books analyzed by means of the standard titration method contained -0.2–2.0% of MgCO_3 (Table 1 in Paper II). Only 52% of the books met the quality standard of alkaline reserve recommended by DIN, which is 0.5–2.0% of MgCO_3 (Hofmann & Wiesner 2011). Hence, alkaline reserve was not sufficiently introduced in many of these books. The XRF analysis of the books treated by the PapersaveTM process exhibited a relatively higher amount of MgCO_3 . Uptake of MgCO_3 ranged from 0.5% to 2.1%, meeting the internal standard (0.3–2.3% of MgCO_3) of the Papersave SwissTM process (Fig. 5 in Paper II). However, after the subtraction of 0.3% of MgCO_3 , which is the average acid content of the corresponding eleven non-deacidified books, 88% of the 40 books gained an alkaline reserve satisfying the DIN recommendation. Thus, the alkaline reserve measured in these books is not entirely sufficient.

3.1.2. Homogeneity

Generally, inhomogeneity of the treatment is determined by measuring alkaline reserve on different spots on a single sheet of paper, not by surface pH (NCW 2004; Hofmann & Wiesner 2011). However, the surface pH could provide a general trend on the homogeneity of the treatment, with appropriate statistical analysis.

The books from the DNB treated with the PapersaveTM process did not show a significant difference between the measured spots; the center and margin of a single sheet from the beginning of the book block and the center and margin of a single sheet from the middle of the book block (Fig. 11 in Paper I) showed similar values. This also applied for the books from the SBB, treated with the PapersaveTM process (Fig. 12a in Paper I). However, books treated with the CSC Book SaverTM process presented a higher surface pH on the margin area of either book block, resulting in a significant difference between the margin at the beginning of the book block and the center of the middle of the book block, according to the Kruskal-Wallis H test¹ even with a probability of 90% (Fig. 12b in Paper I).

The homogeneity of the books deacidified with the PapersaveTM process was examined by means of XRF. Fig. 3-1 illustrates that the alkaline reserve on the center of a single sheet—spot 3 and spot 4—tends to be lower than in the other areas. Applying the t-test, a pair comparison between all data sets proved that spot 3 and spot 7 were significantly different from each other ($p < 0.05$). Spot 3, which is near the spine on the center of the paper sheet, was found to be a “weak” spot, which corresponds to the results from the surface pH measurements. One might consider that the edge area of a paper sheet, e.g., spot 2 in Fig. 3-1, tends to be more acidic and therefore consumes more alkali and lowers the alkaline reserve. However, the inhomogeneity found in this study seems to be related to deacidification parameters such as drying conditions (Kelly & Fowler 1978) rather than to the original inhomogeneity of the paper prior to treatment.

Ninety-three percent of the 40 books could be regarded as homogeneously treated, according to the internal standards of the Papersave SwissTM process, which requires a standard deviation lower than 0.5 (NCW 2004). Since the standard determines “homogenous” treatment when it reaches 95%, the books measured seem to have been treated “nearly homogeneously.” However, 0.5 SD may include a book even with a 1.5% of MgCO_3 difference between the spots in the group of homogeneously treated books (see Fig. 8, right in Paper II). The DIN recommendation does not specify any standard for homogeneity but just states an appropriate method by which to measure it. The inhomogeneity of mass deacidification has been reported in earlier publications (Daniel et al.

¹ Non-parametric statistical test that applies to data not normally distributed. Median and quantiles are tested (StatSoft 2010).

1994; Wagner et al. 2008) and needs to be addressed in future versions of quality recommendations. Completely homogeneous treatment on a mass scale seems to be not easy to accomplish in reality although it may provide relatively homogeneous treatment compared to manual treatment. However, taking into account a close relationship between the amount of alkaline reserve and the long-term efficacy of the treatment as well as the limited diffusion of alkaline reserve, inhomogeneity will eventually produce a “weak” area in the paper. To some extent, each process requires its own quality standards in addition to general tests, considering their characteristic deacidification parameters. Not only is the standard deviation necessary, defining allowable differences between minimum and maximum values will be helpful in aiming at a very homogeneous treatment.

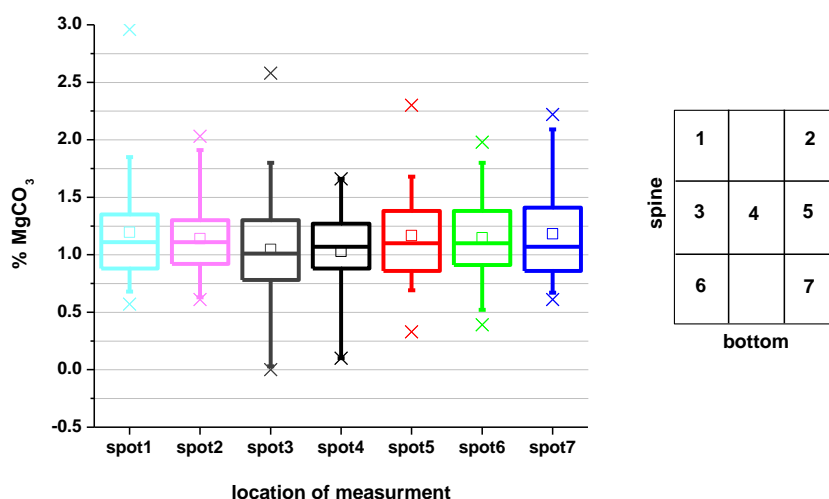


Fig. 3-1. Box plots of % MgCO_3 (XRF) measured on different spots of a single paper sheet. Location of each spot is given in the right figure.

A micron scale of homogeneity of the three different deacidification processes—the PapersaveTM, CSC Book SaverTM, and LibertecTM— was also examined by SEM-EDX. Absolute comparison of these processes is limited, since different papers show different uptake properties of alkaline reserve. In addition, quantitative analysis by SEM-EDX is limited.

No particles of alkaline reserve on the papers treated with the PapersaveTM process and the CSC Book SaverTM process were visible within a given magnification scale, supporting the assumption that they are distributed on a micron scale (Wittekind 1994). By contrast, particle sizes of several 10 microns were observed on the paper treated with

the LibertecTM. The particles of alkaline reserve were of rather irregular shape and size and occasionally aggregated, which may negatively affect an efficient transformation of magnesium oxide to magnesium hydroxide or magnesium carbonate (Zumbühl & Wuelfert 2001; Polovka et al. 2006). Applying magnesium mapping, all samples showed homogenous Mg distribution. Especially, the PapersaveTM process and the CSC Book SaverTM process deposited magnesium compounds finely and homogeneously on the surface. Distribution of alkaline reserve into the paper matrix was better by the PapersaveTM process. The papers displayed a homogeneous magnesium distribution over the entire cross-section of the paper. The CSC Book SaverTM process impregnated alkaline reserve into the paper matrix, but did not fully reach the center area of the cross-sectioned paper. The paper treated with the LibertecTM process hardly showed magnesium in the paper matrix, which again may reduce the efficacy of the treatment (Ramin et al. 2009).

In addition to the homogeneity of alkaline reserve, changes in the surface properties of the papers due to the treatment could also be detected by SEM. SEM images of the papers treated with the liquid immersion systems—PapersaveTM and CSC Book SaverTM—showed relatively more fibers poking out compared to their non-deacidified duplicates, indicating the sizing or calendaring could be slightly disturbed during immersion in the solvents. This phenomenon was found already in deacidification with methyl magnesium carbonate in methanol (Kelly et al. 1977). Intervention of carrier solvents examined in the present study might be minor. However, loss of sizing or calendaring can cause a synergistic effect on the absorption rate of moisture of deacidified papers with alkaline reserve.

3.2. Factors for variations

Reasons why significant variations were found between books and why some books resulted in insufficient pH and alkaline reserve can be numerous: the raw materials of paper, the paper-making process, physical and chemical conditions of the book at the time of deacidification, or the deacidification process itself. In the present study, some of those factors were identified as significant variables that influenced the quality of mass deacidification.

3.2.1. Surface pH vs. year of deacidification and the deacidification process

Statistical analysis using Tukey's test, which is a multiple pairwise comparison of the means, showed no significant difference ($p < 0.05$) between years of deacidification except for 2005 and 2006 (Fig. 9 in Paper I). Surface pH of the books deacidified in 2005 and 2006 was significantly lower than in the rest of the period of deacidification. The years of publication as well as the physical conditions of the books deacidified in 2005 and 2006 could not explain the result, since they were not particularly different in 2005 and 2006. One clear difference of 2005 and 2006 from other periods was the deacidification process. The CSC Book SaverTM process was applied starting from 2004. In 2005 and 2006, all books measured in this study were treated with the CSC Book SaverTM process. Therefore, the CSC Book SaverTM process must have caused a relatively lower alkaline reserve in this period. Another tendency in the process was found in the books deacidified with the LibartecTM process, as expected. Relatively higher surface pH was observed, since the characteristic of the LibartecTM process is the depositing of alkaline reserve onto the surface of paper (Fig. 10 in Paper I). Assessment of the LibartecTM treated papers by surface pH measurement is therefore inadequate.

3.2.2. Surface pH vs. year of publication

Having the pH data separated into two libraries, 84% of the books from the DNB reached pH 7, while only 73% of the books from the SBB met $\text{pH} \geq 7$. One reason the SBB books had a relatively lower percentage of books with successful deacidification can be found in the year of publication, i.e., the age of the books. Books from the SBB were published much earlier than books from the DNB, which were published mostly between 1960 and 1980 (see Fig. 3 in Paper I). A plot of surface pH data against year of publication supports this tendency that younger books obtained a higher surface pH (Fig. 8a and 8b in Paper I). Besides, older books may bring about relatively larger variation in the resulting pH, meaning that control of quality from the mass scale treatment can become more difficult. Therefore, the better the initial state of conditions before mass deacidification, the higher the ratio of success of the treatment, as can be seen in Fig. 3-2.

Why do older books make more problems? In the course of natural aging of paper,

more oxidative functionalities are introduced in cellulose in general. Under alkaline conditions, the carbonyl groups along the cellulose can cause formation of acid degradation products via β -elimination, leading to consumption of more alkali agent. In addition, a relative increase of crystalline regions due to mass loss in the amorphous region during natural aging could also have played a role (Brückle 2011; Whitmore 2011). Accessibility of cellulose to organic solvents can decrease as cellulose crystallinity increases (Loelovich & Leykin 2009). This might hinder the deacidification reagent in penetrating into the paper, and consequently, it will lower the concentration of alkaline reserve in paper.

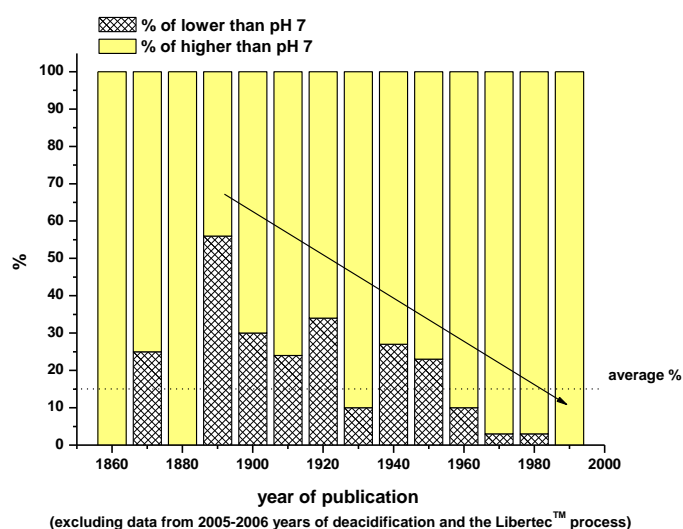


Fig. 3-2. Percentage of deviation from pH 7 in each decade of publication (Data from 2005–2006 years of deacidification and data from the Libertec™ process are excluded).

3.2.3. Alkaline reserve vs. the deacidification process

A reason that only a limited percentage of the books satisfied the standard for alkaline reserve can be found in the deacidification process. Books treated with the CSC Book Saver™ process resulted in the range of -0.2–0.5% of MgCO_3 , indicating that the CSC Book Saver™ process used at that time was the major factor (Table 1 in Paper II). Two of the books treated with the CSC Book Saver™ process contained a negative alkaline reserve, which means that they are still acidic even after deacidification. Fig. 3-3 illustrates how the acidity of the books influences the amount of alkaline reserve left in the paper. The remaining alkaline reserve in the paper is not all of the amount introduced by

the treatment, but the amount after subtraction of the amount consumed for the neutralization of the existing acids. Therefore, a high level of acidity reduces the amount of alkaline reserve left in the paper.

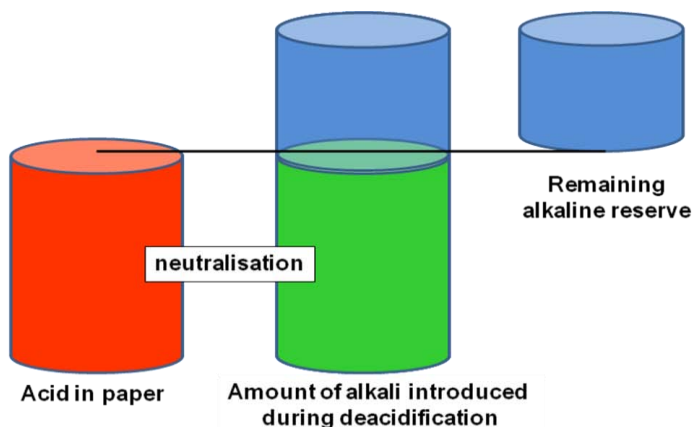


Fig. 3-3. Schematic image of the amount of alkaline reserve finally deposited after deacidification.

Each book has a different acidity. The average acidity of library books in the literature was found to be -0.3% MgCO_3 (Blüher 2006; Andres et al. 2008). A similar average acidity was also found in the 11 non-deacidified books during this study. However, the lowest value of acidity of the sample books was -0.7% of MgCO_3 , and even lower acidities were reported previously (Shahani & Harrison 2002; Blüher 2006). This indicates that the acidity of paper is not negligible for the success of mass deacidification in terms of the amount of alkaline reserve, especially when a relatively low amount of alkaline reserve is targeted by the operating companies of the processes like the case of the CSC Book SaverTM above.

3.3. Reacidification

How fast the deacidified paper returns to being acidic is an important issue for sustainability of mass deacidification. According to Höing (2008), pH and alkaline reserve of a groundwood containing paper treated with the BückeburgTM process seem to be rather stable after 10 years of natural aging. Natural reacidification is difficult to assess because it takes a long time to be detected and there is a lack of detailed documentation about measurement methods of pH and alkaline reserve. In the present

study, the reacidification phenomenon during natural aging was examined with surface pH data, and consumption of alkaline reserve during accelerated aging was tested.

3.3.1. Reacidification determined by surface pH after natural aging

Surface pH data from 51 books, measured before and right after the deacidification, was obtained from the SBB. All books were deacidified with the PapersaveTM process, thus being suitable for tracing changes of pH. Unfortunately, even books deacidified recently (2003–2004) already exhibited a lower pH in 2009 compared to pH measured right after deacidification. Presumably, the lower pH could be a result of systematic errors of the surface pH measurements and not of reacidification. However, the books deacidified in 1998–1999 decreased their surface pH by more than 1.2 units on average until 2009, which is a much higher reduction than the books deacidified in 2003–2004, which showed a reduction of the average of only 0.4 pH units (Fig. 3-4 below and Fig. 13 in Paper I). Thus, there is a trend that the earlier the book is deacidified, the lower is the pH measured in 2009, which leads to the conclusion that signs of reacidification of deacidified paper are visible after more than ten years of natural aging. An absolute rate of reacidification is not given here, as measurement parameters of the analysis right after deacidification could not be confirmed.

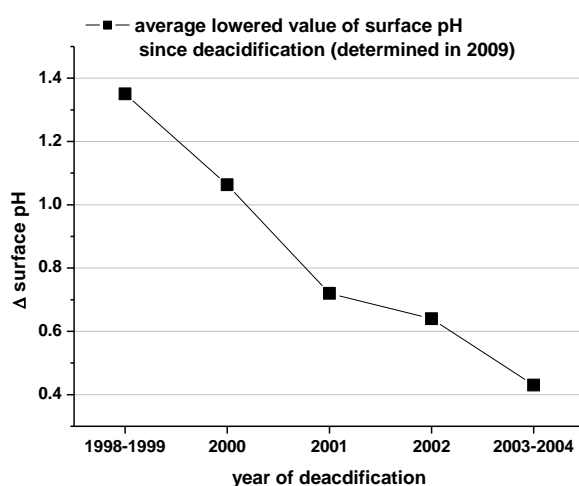


Fig. 3-4. Average lowered values of surface pH between right after deacidification and the current year (2009). The longer the natural aging period after deacidification, the higher the decrease in surface pH.

3.3.2. Reacidification examined by alkaline reserve

As no alkaline reserve data from previous measurements were available, a consumption rate of alkaline reserve was examined during accelerated aging.

Discussing absorption of VOCs and air pollutants by alkaline reserve, many studies emphasized that the sorption rate of atmospheric pollutants such as SO₂ or NO₂ increases significantly when paper contains an alkaline reserve (Atherton et al. 1973; Gurnagul & Zou 1994; Guttman & Blair 1996; Havermans 1995; Johansson et al. 2000; Zou et al. 1998; Zou 2004). A preliminary study of acetic acid vapor exposure also showed a similar tendency. Percentage weight change of the deacidified paper was much more pronounced after exposure to acetic acid vapor, compared to non-deacidified paper. Hence, the deacidified paper absorbed more acetic acid vapor (Fig. 3-5). The amount of alkaline reserve is proportionally correlated with weight change, i.e., uptake of acetic acid vapor for an identical paper specimen in general.

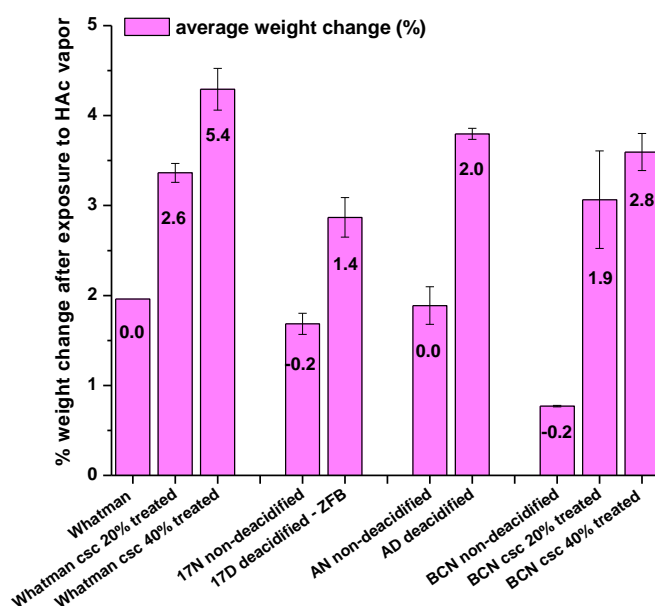


Fig. 3-5. Weight change (%) of deacidified papers and their non-deacidified duplicates after 4 weeks of exposure to acetic acid vapor with a dose of 400 mg/m³. The data represent average values of two or three different specimens with a standard deviation presented in the error bar. A number in each bar indicates % MgCO₃ determined by titration.

A higher sorption of volatile organic vapors found in deacidified paper must be related

to the amount of consumption of alkaline reserve during accelerated aging. The amount of alkaline reserve decreased more quickly in deacidified paper compared to that in non-deacidified paper (Fig. 3-6). During accelerated aging, some acidic degradation products are expected to form only in deacidified paper via β -elimination to a small extent. Detection of relatively less acetic acid from deacidified paper (Doering 2007) indicates that consumption of alkaline reserve can surely be expected by neutralization reactions during aging. Therefore, a relatively quicker consumption rate of alkaline reserve of deacidified paper found in Fig. 3-6 is not a surprise. A higher consumption rate of sample no. AD, which contained a higher amount of alkaline reserve, however, could be attributed to a higher sorption rate of acids formed during accelerated aging by alkaline reserve. It means that reacidification of deacidified paper will significantly speed up under polluted environmental conditions.

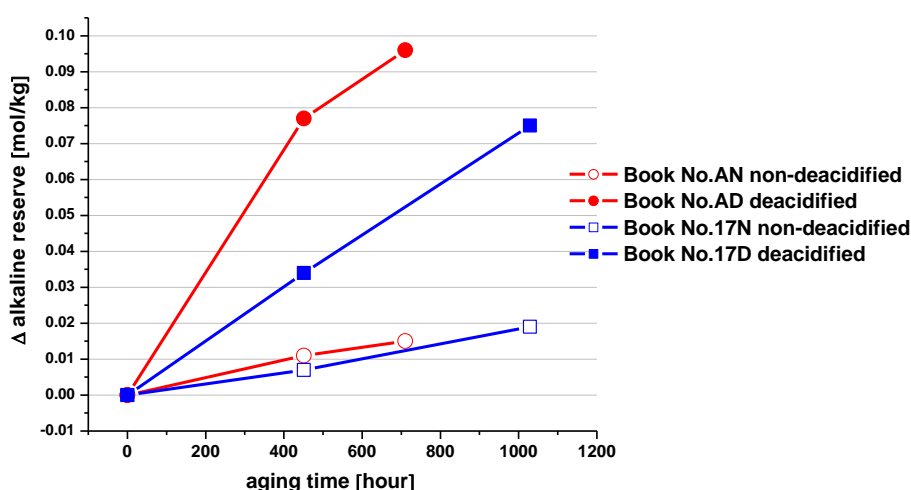


Fig. 3-6. Lowered amount of alkaline reserve in deacidified papers and their non-deacidified duplicates during accelerated aging. The amount of alkaline reserve was determined by the standard titration method (ISO 10716: 1994 (ISO 2003a)).

3.4. Influence of mass deacidification on original books during natural aging (Paper III)

According to the results from the analysis of alkaline reserve, books often contained a lower amount of alkaline reserve as required by e.g., DIN recommendation or the internal

quality standard of the Papersave SwissTM process. Among the samples analyzed, only a few books were found to possess a higher amount than the amount the international and national standards for permanence of paper require. One reason is, of course, to carry out a “cost”-effective treatment. Another reason is to avoid an adverse effect, that is, alkali-induced degradation of cellulose. As naturally aged book papers are subjected to deacidification, β -elimination reaction triggered by oxidative functionalities of cellulose is a major concern. Several studies with oxidized model pulps or papers have demonstrated the possibility of cellulose degradation due to a deacidification treatment (Kolar & Novak 1996; Bogaard & Whitmore 2001; Bogaard et al. 2005; Malesič et al. 2002; Stephens et al. 2009). The risk of cellulose degradation during deacidification depends on the oxidation state of the paper and the applied pH. A question is whether it actually occurs in the original book papers treated in mass deacidification or not. In order to find this out, 25 deacidified book papers and their non-deacidified duplicates were analyzed by GPC after labeling of carbonyl groups with CCOA. The conditions of the deacidified books varied in terms of year of publication (1893–1992) and year of deacidification (1994–2006) as well as the resulting surface pH (pH 6–9.3).

3.4.1. Influence on molecular weight

Weight-average molar masses of all deacidified book papers were comparable to those of their non-deacidified duplicates except for two samples. The two deacidified sample books had an Mw that was more than 10% lower compared to the respective non-deacidified duplicate; no distinctive similarities could be found. One book with surface pH of 7.1 was originally published in 1893 and contained a content of lignin detectable with FT-IR analysis using ATR, while the other book with surface pH 9.0 was published in 1970 and contained no detectable amount of lignin. They seem to be outliers, not degraded due to mass deacidification treatment if considered unknown environmental conditions and frequency of usage undergone by the deacidified papers and their non-deacidified duplicates. The t-test: paired two-sample for means still proved no significant difference ($p < 0.05$) between deacidified samples and their non-deacidified samples, even after including these two samples.

Again, no significant difference was found when only 11 samples that were deacidified more than 10 years ago were compared to their non-deacidified duplicates (Fig. 4 in paper

III). No difference between two sample sets, which have undergone 10 years of natural aging at least after mass deacidification, indicates that mass deacidification does not induce cellulose degradation in original books on the one hand, but it does not exhibit a long-term effect of mass deacidification yet, after natural aging of 10 years under library conditions.

The outcome from Mw of the original book samples is solely opposite to the chemically oxidized model pulp. The oxidized bleached sulfite pulp had a significantly decreased Mw after an identical mass deacidification process that was applied to the original books (Fig. 2 in Paper III). The extent of Mw loss (%) did correlate with its initial oxidation state, i.e., the total carbonyl content (Fig. 3 in Paper III). A distinct decrease of the carbonyl groups after deacidification was also visible. Therefore, it is certain that the mass deacidification treatment can cause β -elimination in the oxidized model pulp, resulting in severe cellulose chain scission as well as the consumption of along-chain carbonyl groups due to the reaction. The reason for this different behavior is discussed in the next paragraph.

3.4.2. Influence on carbonyl groups

By analyzing the carbonyl group contents of the original book samples, a typical sign of β -elimination reaction could be detected, as a decrease in the carbonyl contents was visible. The contents of along-chain carbonyl groups of deacidified book samples were significantly lower than those of their non-deacidified duplicates, according to the t-test: paired two-sample for means ($p < 0.05$) (Fig. 6, right, in paper III). This tendency could not be proved statistically when the total carbonyl group contents were compared. It is because the extent of decrease in the along-chain carbonyl groups, i.e., of β -elimination, was not large, and the reducing end groups, which are part of the total carbonyls, contribute more to the overall value compared to along-chain carbonyls. Since β -elimination was found in the deacidified book papers, a question arises: Why did the mass deacidification treatment not cause a decrease in molar mass in original book samples? Original book papers are often more oxidized than the chemically oxidized model pulp discussed above. Therefore, a theory that the more the oxidation, the larger the degradation of cellulose from oxidative peeling reaction, cannot be used to explain the trend in original book papers.

As previously discussed in the introduction (1.4 Alkaline degradation of cellulose), when β -elimination is triggered by keto or aldehyde groups along the cellulose located in the chain ends, it will not bring about significant cellulose degradation. The reason is that

only a few AGU units are cleaved off, but it will reduce the carbonyl content, mostly keto groups along the chain. This could be a reason why β -elimination was not accompanied by a significant chain scission.

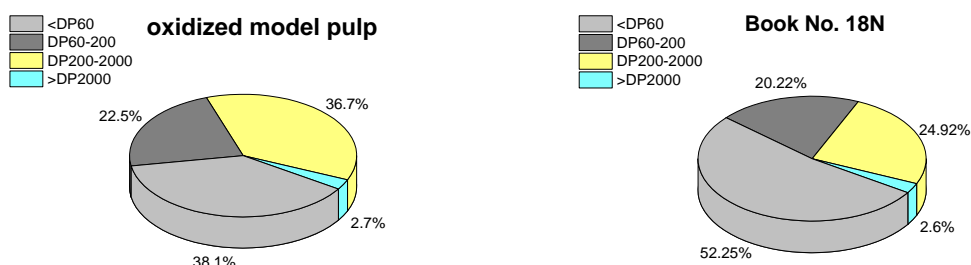


Fig. 3-7. Percentages of total carbonyls in the respective DP regions of an example book (No. 18N) and an oxidized model pulp. Total carbonyl group contents were 53.7 $\mu\text{mol/g}$ for No. 18N and 45.9 $\mu\text{mol/g}$ for the oxidized model pulp.

In addition, even if carbonyl groups are present in the middle of a cellulose chain and cause β -elimination, when the chain is already too short, β -elimination reaction will not affect Mw remarkably. As illustrated in Fig. 3-7, the oxidized model pulp contained a large portion of the carbonyl groups in the region of DP 200–DP 2000, whereas more than 50% of the carbonyl groups are located in the low DP region for the book sample. The other book samples share this trend when averaging the values for all books investigated. Therefore, β -elimination occurs more in the short cellulose chains and at the chain end in the naturally-aged book papers, unlike the oxidized model pulp, and eventually brings about fewer chances for severe Mw loss.

3.5. Aging behavior of deacidified paper during accelerated aging (Paper IV)

Sustainability of mass deacidification is difficult to judge with deacidified books that have undergone only up to 15 years of natural aging, since they presented neither degradation nor stabilization compared to non-deacidified counterparts. In order to further investigate a long-term effect of mass deacidification on book paper, original book papers were subjected to accelerated aging. Although degradation mechanisms of

paper under the conditions of accelerated aging are not exactly the same as under natural aging, accelerating endothermic reactions in paper at an elevated temperature is helpful to understand relative degradation rates (Porck 2000). Uncertainty of accelerated aging could be reduced by applying the exact same aging conditions to a sample set of deacidified paper and its non-deacidified paper, together with a reference paper composed of pure cellulose, which would play a role as an internal standard for the given aging conditions.

3.5.1. Influence of alkaline reserve on molecular weight

During accelerated aging, three main degradation mechanisms are expected to occur in deacidified papers (see Fig. 2 in paper IV). β -elimination starting from oxidized functionalities present in naturally aged papers takes place. A relatively slow oxidation reaction under alkaline condition via radical formation can occur and then subsequently promote the β -elimination. Additionally, acid hydrolysis is still possible when alkaline reserve is not sufficiently or homogeneously distributed into the paper matrix, being unavailable to react with acidic compounds formed during aging.

Analysis of carbonyl groups and molecular weight of a variety of samples after accelerated aging could verify major degradation mechanisms of deacidified papers. Papers successfully deacidified, e.g., sample no. 1D in Fig. 3-8, showed a reduced degradation rate of up to three times compared to their non-deacidified duplicates. In contrast, books treated insufficiently or inhomogeneously gained almost no or relatively little beneficial effect on cellulose stability. In Fig. 3-8, sample no. 4D, treated with the LibertecTM process, displayed a similar degradation rate to the sample no. 4N non-deacidified duplicate. Despite about 0.3% of MgCO_3 and surface pH 8.8 determined in 4D, the fact that the deacidification treatment was not beneficial can be explained by the distribution of the alkaline reserve. In this same sample, almost no penetration of alkaline reserve into the paper matrix and relatively large and irregular magnesium oxide on the surface were previously ascertained by SEM-EDX analysis (see 3.1.2. Homogeneity). This leads to a first conclusion that fine and homogeneous deposit of alkaline reserve is one of the key factors that enhance cellulose stability by deacidification. In other words, the alkaline reserve can efficiently react with acids formed during aging, reducing acid hydrolysis when they are readily available for acids.

In case of sample no. 3D in Fig. 3-8, again, it did not reduce the degradation rate to a large extent after the treatment, since the amount of alkaline reserve left in the paper was insufficient. It still contained “negative % MgCO_3 ,” -0.2% of MgCO_3 indicating that the paper is still acidic after deacidification. Its counterpart, 3N, was extremely acidic (-0.7% of MgCO_3); the uptake of alkaline reserve was not even enough for neutralization of existing acids. One reason that the PapersaveTM process brought about more benefits is that it deposited more alkaline reserve (Table 1 in Paper IV). Therefore, a sufficient amount of alkaline reserve was found to be another highly important factor to increase cellulose stability on the long run. In relation to the amount of alkaline reserve, more data will be discussed in 3.6.3. Alkaline reserve vs. cellulose analysis.

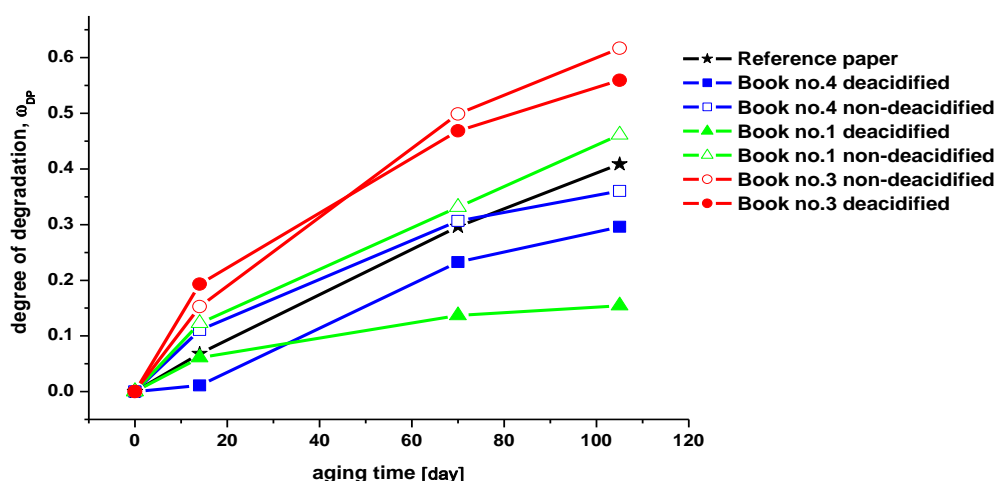


Fig. 3-8. Rates of cellulose degradation of deacidified books and their non-deacidified duplicates, plotted as accumulated percentaged DP loss. Sample 1D was successfully deacidified according to the DIN recommendation (Hofman & Wiesner 2011); sample 4D met the standards, but alkaline reserve observed mainly on the surface of paper; sample 3D simply did not meet the standards.

3.5.2. Influence of alkaline reserve on carbonyl groups

When carbonyl groups were measured, the degradation mechanisms of the deacidified papers, in comparison with their non-deacidified papers, could be elucidated in more depth. Most deacidified book samples decreased the content of total carbonyl groups after accelerated aging. On the other hand, their non-deacidified duplicates gained it significantly (Fig. 4, right, in paper IV). Dominant hydrolytic degradation took place in non-deacidified papers, increasing REGs by chain scission, which corresponded to an

increase in total carbonyl groups during accelerated aging, like sample no. 8N in Fig. 6 in Paper IV. In the case of deacidified papers, the formation of REGs was significantly suppressed thanks to alkaline reserve. However, along-chain carbonyls, i.e., ketos/aldehydes along the chain, were found to decrease during aging, implying they are consumed by β -elimination reactions. It should be noted that even non-deacidified papers tended to decrease along-chain carbonyls under the conditions of accelerated aging applied in this study. This seems to be because accelerated aging conditions induced hydrolytic degradation dominantly, but suppressed formation of novel oxidative functionalities. Consequently, existing carbonyl groups in non-deacidified papers might have been consumed by further oxidation or were not measured any longer, due to fragmentation by chain scission. Nevertheless, along-chain carbonyl groups decreased more significantly in deacidified papers than in non-deacidified papers (Fig. 7 in paper IV). Therefore, β -elimination occurs during accelerated aging in deacidified papers, which can be regarded as a side effect of mass deacidification. However, β -elimination found in deacidified papers did not cause severe chain scission to an extent influencing the Mw. The decreased amounts of along-chain carbonyl groups after aging in deacidified papers show correlation neither with initial carbonyl groups, i.e., initial states of oxidation of the book papers before aging ($R^2=0.2694$), nor with Mw loss (%) after aging ($R^2=0.1139$). Therefore, β -elimination seems to take place mainly either at chain ends or at short chains, as described in Paper III.

According to two different model book papers impregnated with different amounts of an alkaline reserve, the higher the amount, the more the decrease in along-chain carbonyls groups after aging (Fig. 8, right in paper IV). Therefore, a higher amount of alkaline reserve can cause more β -elimination. However, decreased content of along-chain carbonyl groups due to β -elimination did not exhibit a direct correlation with % Mw loss. Even with a higher amount of alkaline reserve than the upper limit (2.0% of MgCO_3 , i.e., 0.48 mol/kg of alkali reserve approx.), there was no evidence that β -elimination occurs to an extent that affects Mw negatively, cancelling out all benefits from alkaline reserve. Instead, each book poses a threshold of alkaline reserve amount that does not improve cellulose stability any more.

3.6. Relation between evaluation criteria (Paper I, II, and IV)

Measurement methods of pH and alkaline reserve vary depending on the availability of samples or analytical instruments. In case of test papers, destructive measurements are possible, according to the ISO standard methods such as pH by cold extraction (ISO 6588-1:2005 (ISO 2006a)) and alkaline reserve by titration (ISO 10716: 1994 (ISO 2003a)). However, taking samples from original papers is limited; therefore, they are often monitored by surface pH and/or alkaline reserve determined by Mg content. Thus, relationships between the criteria of quality assessment or between different measurement methods need to be discussed.

3.6.1. Surface pH

Surface pH is currently the only parameter that is readily accessible in libraries and archives. A question is how much we can depend on surface pH data for the assessment of the quality of mass deacidification. Hence, the relation of the surface pH to the amount of alkaline reserve (% w/w MgCO_3) was examined in this aspect.

Surface pH correlated well to the amount of alkaline reserve when the amount had a negative value, i.e., was acidic. However, it could not exactly reflect the amount of alkaline reserve after deacidification, which corresponds to the literature (Saverwyns et al. 2002; Kelly 1989) (Fig. 14 in paper I). A surface pH near 7, which is a threshold for successful deacidification treatment, often implies a lower amount of alkaline reserve than the amount required from the quality standards. Therefore, the reliability of surface pH is limited for an assessment of sufficient amount of alkaline reserve quantitatively, due to the reasons that are described in the introduction.

However, when surface pH data are collected from an extensive number of papers, surface pH could identify the general performance of deacidification with the assistance of statistics, which correspond to data from alkaline reserve. In addition, taking into account a good correlation of surface pH with the amount of alkaline reserve in the acidic region, surface pH can be used for an estimation of how much alkaline reserve is consumed during mass deacidification. In any case, establishment of more detailed standard procedures of the measurement are needed to make surface pH data more valuable.

3.6.2. Measurements of alkaline reserve: Titration vs. XRF

Since thus far, instrumental analysis of alkaline reserve measures only the Mg or Ca ions and not the actual Mg or Ca alkaline compounds, % MgCO_3 from XRF measurement was plotted against % MgCO_3 determined by titration (ISO 10716: 1994 (ISO 2003a)) to check whether a correlation exists. It should be noted again that alkaline reserve of the PapersaveTM treated books determined using XRF is the amount of uptake and was calculated on three assumptions that were previously described (see 1.5.2 Alkaline reserve-XRF).

As seen in Fig. 4 of paper II, % MgCO_3 determined by XRF correlated with % MgCO_3 determined by titration, exhibiting a similar trend. However, % of MgCO_3 determined by XRF is often significantly higher compared to the value obtained by titration, and it tends still to be higher than the values determined by titration even after subtracting the average acid content, i.e., -0.3 % of MgCO_3 , of original books before deacidification. In some cases, a significantly lower amount of MgCO_3 than the value determined by the titration was detected by XRF, which could be explained by a change in uptake ratio of Ti and Mg or less correlation to the % MgCO_3 calibration versus Mg constituent. Therefore, alkaline reserve determined by XRF might overestimate the actual amount of alkaline reserve in general. A larger RSD is expected from the instrumental determination of Mg constituent when it is applied to original books, since the assumptions may not always be true for all original book papers, and different physical and chemical properties of paper can also cause variations. This trend should be reflected in the quality standard.

3.6.3. Alkaline reserve vs. cellulose analysis

Current recommendation by DIN and the internal standard for the Papersave SwissTM process proposed 0.5–2.0% of MgCO_3 to be deposited after mass deacidification for test papers. Since no international standards for deacidification are available, the “success” of the treatment in terms of alkaline reserve only depends on DIN recommendation, at least in Germany, without questioning. Whether this amount is optimum for the long-term stability of paper or how it was determined seems not to be clear. According to the present study with original book papers, ω_{DP} after applying accelerated aging

proportionally correlated with the amount of alkaline reserve determined by titration ($R^2 = 0.71092$) (Fig. 5 in paper IV). The correlation is found from the acidic region to the alkaline region, which means that no other major degradation mechanisms play a role when the paper becomes alkaline. β -elimination detected by a decrease in along-chain carbonyls was not severe enough to influence Mw. Therefore, a long-term beneficial effect of mass deacidification is highly dependent on the amount of alkaline reserve.

The model book papers contained various amounts of alkaline reserve. It could be demonstrated that the higher the amount of alkaline reserve is, the better is the cellulose stability upon accelerated aging in general. However, it was found that there is a certain limit for the amount of alkaline reserve. Above this limit, no additional beneficial effect of alkaline reserve on cellulose stability is observed. The threshold depends on the book. Model book paper 1 showed a threshold lower than the upper limit of DIN recommendation, but model book paper 2 still obtained the benefits from a much higher amount. Nevertheless, despite the threshold, exceeding the limit does not necessarily mean that the paper will be harmed. Therefore, the current recommended amount for alkaline reserve should be revised towards a higher range.

It is worth addressing again that the conclusions on the amount of alkaline reserve are based on the fine and homogeneous distribution of alkaline reserve into the paper matrix as well as on the surface, which should be included in the quality standards for mass deacidification.

4. Conclusions

The summary of the assessment of books treated by mass deacidification processes from 1994 to 2006 is as follows. About 80% of the 443 book papers satisfied the surface pH of ≥ 7 . No statistically significant trend was found by the year of deacidification from the books treated, except 2005 and 2006. The books treated in 2005 and 2006 showed a lower surface pH, which was mainly caused by a change in the deacidification process to the CSC Book SaverTM process from 2004 onward in both libraries. The results from alkaline reserve measurement follow the findings from the surface pH measurements. According to the alkaline reserve determined by the standard titration method, only 52% of 21 books met the current DIN recommendation (0.5–2.0% of MgCO_3). Most of the books not satisfying the recommendation contained a lower amount of alkaline reserve than the recommended amount. The CSC Book SaverTM process was mainly responsible for the lower amounts. XRF analysis of Mg content in 40 books that were treated only with the PapersaveTM process demonstrated that 88% of the books met the DIN recommendation after subtraction of the average acid content of non-deacidified book papers. The PapersaveTM process performed relatively better than the other processes, but still needs improvement.

In addition, another important factor of the process is the year of publication, which also influences surface pH and alkaline reserve after mass deacidification. Data obtained from earlier years of publication, i.e., older books, tend to be lower, and fluctuation among books was higher. Hence, the efficiency of the treatment is lower when books are older.

In terms of homogeneity of alkaline reserve, 93% of 40 books treated by the PapersaveTM process showed a standard deviation of 6–7 spots in a single sheet below 0.5, which is based on the internal standard for the Papersave SwissTM process. The area of the center or close to the spine in the middle of a book block tended to be lower, according to surface pH measurements as well as alkaline reserve determined by XRF. SEM-EDX analysis on a local area demonstrated fine and homogenous distribution of alkaline reserve into the paper matrix as well as on the surface of the papers treated with the PapersaveTM and the CSC Book SaverTM. However, the LibertecTM-treated paper exhibited magnesium substances in uneven sizes and shapes on the surface and almost no

trace of impregnation of Mg substances into the paper matrix, which eventually largely reduced the efficacy of the treatment during accelerated aging.

Reduction of hydrolytic degradation of cellulose in deacidified papers could clearly be detected after accelerated aging compared to their non-deacidified duplicates. A long-term beneficial effect of mass deacidification on the cellulose stability highly depends on the distribution and the amount of alkaline reserve. Only sufficient amounts and a fine distribution of alkaline reserve throughout the paper matrix enhanced the effect of the alkaline reserve as a barrier to acid attack.

Concerning alkaline degradation of cellulose due to mass deacidification treatments, a decrease in along-chain carbonyl groups was found after treatment as well as after accelerated aging, indicating that β -elimination indeed occurs. However, naturally aged book papers exhibited no loss of molecular weight after treatment or during more than 10 years of natural aging. The phenomenon of a slight decrease of keto/aldehyde along the chain but no Mw loss led to the conclusion that β -elimination takes place mostly at the chain ends and at short cellulose chains. An accelerated aging study gave similar results. Decrease in along-chain carbonyls found in deacidified papers did not correlate with Mw loss after accelerated aging. Degradation of deacidified papers during accelerated aging was overruled by the amount of alkaline reserve without influence of β -elimination, indicating that a major degradation mechanism is still acid hydrolysis, even after deacidification. According to the model book papers impregnated with a different amount of alkaline reserve, more alkaline reserve can induce more decrease of along-chain carbonyl groups, i.e., more β -elimination. However, even a higher amount of alkaline reserve than the upper limit of the current DIN recommendation did not lead to the extent of cancelling out all beneficial effect of mass deacidification on cellulose stability. Only a threshold of alkaline reserve that does not enhance cellulose stability any more was found, depending on the papers.

A sign of reacidification of deacidified book papers within a period of ten years of natural aging was visible when surface pH data obtained from surface pH measurements right after deacidification to those measured in 2009 were compared. The accelerated aging study also showed that the rate of decreasing alkaline reserve is higher in deacidified papers than in non-deacidified papers, which could be caused by a higher absorption of acidic degradation products. An adequate system enabling libraries to

evaluate the reacidification in the course of natural aging should be established.

Criteria for assessment of mass deacidification carried out in this study were related to each other. Especially, the amount of alkaline reserve under the condition of assurance of its fine and homogeneous distribution throughout the paper matrix is a good indicator of how effective the treatment is on cellulose stability for the long-term. Surface pH cannot be used as a single parameter for evaluation of mass deacidification. The borderline surface pH around pH 7 often indicates a lower amount of alkaline reserve than the amount required by the current DIN recommendation. On the other hand, trends resulting from surface pH measurements corresponded to those from alkaline reserve. Therefore, with an extensive number of samples and statistical analysis as well as more detailed standard procedures for measurement, surface pH may still provide meaningful data if used as a simple and low-cost technique without taking a sample. Cellulose analysis, with a sensitive tool for the measurement of oxidative functionalities, is absolutely necessary to get a deeper insight on degradation mechanisms of deacidified papers and non-deacidified papers and to judge the long-term beneficial effect of mass deacidification before and after accelerated aging.

Not to mention that the recommendations by DIN for quality of mass deacidification need to be more detailed and specific; the absence of quality standards from DIN for original book papers made it difficult to conclude the “success” of the treatments examined in this study. Based on the results from cellulose analysis after accelerated aging, a higher amount of alkaline reserve than given in the DIN recommendation should be taken into consideration for future standards and protocols. The standard to assess a micro-scale distribution of alkaline reserve into the paper matrix as well as at the surface should be included, since it was one of key factors in improving the efficacy of the treatment.

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Paper I

**Sustainability of mass-deacidification – Part I:
Concept, selection of
sample books, and pH-
determination**

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Sustainability of Mass Deacidification. Part I: Concept, Selection of Sample Books and pH-Determination

by Kyujin Ahn, Ute Henniges, Agnes Blüher, Gerhard Banik and Antje Potthast

Abstract: The German National Library (Deutsche Nationalbibliothek, DNB) and the Berlin State Library (Staatsbibliothek zu Berlin, Stiftung Preussischer Kulturbesitz, SBB) applied mass deacidification processes using the Papersave™, the Libertec™, and the CSC Book Saver™ process to parts of their collections from 1994 (DNB) and from 1998 (SBB) until now. The sustainability of mass deacidification was scientifically evaluated by analysis of 443 deacidified books from both libraries. pH, alkaline reserve and the molecular structure of cellulose were investigated to assess if and to what extent the treatment had improved the overall stability of the paper. This first part of the paper includes results of surface pH measurements and discusses how surface pH, with all its known limitations, can be used as an easily accessible and valuable parameter to determine whether mass deacidification of books was effective. Books treated in the period from 1994 to 2006 were analysed; about 80% of them had a surface pH of ≥ 7 . No distinctive trend by year of deacidification could be discerned except the years 2005 and 2006 which showed a comparatively lower pH. Comparing the pH measured in 2009 with the values measured directly after deacidification, indications of natural re-acidification could be observed in books treated during earlier years. Especially the surface pH measured in older books was found to be slightly lower and more varied.

Zusammenfassung/résumé at end of article

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1. Introduction

The ‘KUR Programm zur Konservierung und Restaurierung von mobilem Kulturgut’ (Programme for the Conservation of Moveable Cultural Assets) was established by the Federal Cultural Foundation (Kulturstiftung des Bundes) and the Cultural Foundation of the German States (Kulturstiftung der Länder) in 2007. This programme was designed to support projects that aim at preservation of objects which are seriously endangered by deterioration. It also explicitly encourages the collaboration between research institutes and collections on a national and international level (KUR 2008). The project ‘Sustainability of mass deacidification of library collections’ was launched as a KUR project in 2008 as a cooperation between four institutions: the German National Library (Deutsche Nationalbibliothek, DNB), the Berlin State Li-

brary (Staatsbibliothek zu Berlin, Stiftung Preußischer Kulturbesitz, SBB), the Chemistry Department at the University of Natural Resources and Life Sciences Vienna (BOKU Wien), and the Swiss National Library (SNL) in Bern.

Both the German National Library (DNB) and Berlin State Library (SBB) had changed their mass deacidification systems during a period of sustainability assessment that lasted from 1994 to 2006. From 1994 until 2004, the main provider for deacidification services for both libraries was the Zentrum für Bucherhaltung, Leipzig (ZFB) that exclusively used the Papersave™ process, which is also known as the ‘Battelle process’. It is based on liquid infiltration of a solution of titanium-magnesium ethoxylate in hexamethyldisiloxane (HMDO) into the books. From 1998 to 2000, some parts of both collections were processed by Battelle in Eschborn (Germany) using an identical process. Furthermore, other parts of the SBB collection underwent deacidification with the Libertec™ process in Nürnberg (Germany), by which a sub-micron magnesium oxide dispersed in a dry air stream is applied to the books.

From 2004 onwards, both collections were treated exclusively by the CSC-Book Saver™ process which is provided by the Preservation Academy Leipzig (PAL). This process is based on the infiltration of books and archival documents with a solution of carbonated magnesium-propylate dissolved in *n*-propanol and hexafluoropropane as an inert carrier liquid.

Overall, the KUR project aimed at the scientific evaluation of long-term advantages of mass deacidification that had been applied to these two collections in the past. The main focus was the assessment of the treatment’s long-term benefit with regard to pH stability, the percentage of alkaline reserve deposited in the paper structure, and molecular stability of cellulose, the most important bio-polymer in paper. In Part I, we present results of pH-determination and their relation to the alkaline reserve.

2. Perspectives for controlling deacidification quality

Determining the quality of mass deacidification treatments is a difficult task for clients and providers. This complication is mainly due to a lack of proper instrumental procedures that offer the required accuracy. No efficient processing techniques are yet available for this purpose. Chemical tests such as pH or alkaline reserve determinations, or physical tests such as tensile strength after one defined fold or zero span tensile strength provide only limited information and, being destructive, require extensive sample material. Hendriks stated already in 1994 that none of these tests allows the prediction of the chemical stability or ageing properties of paper (Hendriks 1994).

The analysis of volatiles formed during the natural ageing of paper constitutes an innovative approach for analysis of paper degradation in general. Buchbauer et al. (1995) were the first to identify the volatiles released from old paper, i.e. the odour of old books, by means of GCMS. Doering (2001, 2007) succeeded in identifying furfural and acidic acid as marker substances indicative for acid hydrolysis and oxidative degradation of paper before and after deacidification. Sampling of volatile products by SPME (solid phase micro extraction) is non-destructive and permits through quantification of indicator substances a direct insight about the degradation of various historic papers. Further, this procedure has been applied successfully to evaluate and monitor the efficiency of commercially available mass deacidification systems (Doering 2007). However, the analytical procedure has not yet been developed to the point where it can be employed as a low-cost in-house test procedure.

Near infrared spectroscopy (NIR) is another promising technique to address the state of deterioration of paper. A mobile instrument (SurveNIR) is already marketed. This system uses near and mid-range infrared spectroscopy after data processing with multivariate analysis. It can be operated in-house and enables conservators to easily determine the condition of naturally aged papers with regard to pH, DP of cellulose, lignin content as well as mechanical parameters. The correct interpretation of the data gathered with this instrument depends on their correlation with data gained from chemical, physical and spectroscopic analysis. The use of NIR, in other words, requires a standard created beforehand from as many reference samples as possible and the accuracy of data gained by the traditional methods of analysis (Trafela et al. 2007). In principle, the system has demonstrated its applicability in a number of prominent European collections (Lichtblau et al. 2009), but the accuracy of the results is still limited due to the enormous variety of historical papers which require a broader basis of reference materials to further improve the NIR analytical precision (Blüher 2011). Also, NIR cannot yet be used with deacidified paper as these have not yet been included into the calibration.

In a related study, the determination of volatiles released by paper during ageing was correlated with its rosin and lignin content, the amount of carbonyl groups present, the DP and pH using multivariate calibration with the aim to better understand the relations between these parameters (Strlič et al. 2009). The sampling in this case was based on SPME followed by GCMS and suffers from the same drawbacks like the conventional SPME technique because the equipment is not compatible with low-cost in-house requirements.

In sum, it can be said that currently, both the NIR and SMPE techniques are not yet fully translated into conservation practice, but both offer potential in that they can be used to characterize either the condition of a piece of paper or the improve-

ment of its permanence as result of a deacidification intervention through one or more significant products formed during paper degradation; this is of decisive importance (Hendriks 1994).

Until now, the quality of a mass deacidification treatment and its sustainability have been evaluated only by two parameters, the pH of the paper after treatment and the concentration of the so-called alkaline reserve deposited in the paper structure. The current recommendations according to DIN (Hofmann and Wiesner 2011) and the Swiss Quality Standard in its current version (Nitrochemie Wimmis AG 2004) still require the use of traditional analytical techniques, such as surface or extraction pH and the determination of alkaline reserve according to ISO (ISO 10716: 1994).

2.1 Surface pH

Surface pH is a common method of evaluating the result of mass deacidification of library and archive materials. This is mainly due to the fact that no other low-cost method of evaluation requiring only few personnel resources can be applied in-house in libraries and archives. Further, it is a technique that does not require sampling, and although it can cause water stains on and distortions of the original paper, it is regarded as “non-destructive”. However, it is well known that the pH concept does not provide information about the acidity¹ or alkalinity² of paper but only about the actual concentration of hydronium ions, that get dissolved in the water volume applied. The paper’s composition, its surface characteristics, and its absorbency therefore are of decisive importance when a paper’s pH must be measured.

At first sight, the determination of the pH on the surface of the paper seems to be a relatively easy task, especially if compared to the more laborious and destructive extraction procedures. Flat surface electrodes are easily available from a number of suppliers and standard pH meters can be used. In addition, a standardized method has been published by TAPPI (TAPPI 529 om/99). However, the data collected by different research groups and library staff are hardly comparable. Even within a single batch of samples, considerable differences in the pH have been observed. The reasons for this phenomenon are manifold. Differences may be caused by inhomogeneities of paper and by the inaccurate definition of the volume of water to

¹ acidity is the neutralizing capacity of acid compounds present in paper that in an aqueous environment release hydronium ions (H_3O^+) that neutralize hydroxide ions (OH^-)

² alkalinity is the neutralizing capacity of alkaline compounds present in paper that in an aqueous environment release hydroxide ions (OH^-) that neutralize hydronium ions (H_3O^+)

be applied in order to extract hydrogen ions from paper and to enable their migration to the measurement device. In addition, material parameters of papers, such as density of the paper structure, presence of coatings and sizing agents which influence water absorbency and penetration are not taken into consideration.

While pH measurement of paper according to the cold and hot extraction standards (TAPPI 509 and TAPPI 435 respectively) require extraction of 1 g of sample in 70 ml of water (TAPPI 2004), the TAPPI 529 surface pH measurement of paper defines the amount of water to be applied to the paper surface as 'a drop', which depends on what kind of pipette or syringe is used. It also recommends at least 10 minutes of immersion for the flat electrode head in the water drop, which means that the electrode head has to be placed on the wetted area of a paper piece not described in its dimension; nor is the allowable drift range before each reading defined (TAPPI 2004). Due to the vague procedural protocol, the pH readings are not easily reproducible, especially when one considers also the variation introduced by different operators. It would be highly desirable to refine this TAPPI procedure by establishment of a more detailed protocol that improves accuracy and reproducibility.

Further, surface pH measurement using a flat electrode may mislead the electric potential of the electrode due to the charged fibres and particles on the paper surface (Strlič et al. 2004). Many experimental comparisons between surface pH measurement and cold extraction pH measurement have been carried out in the recent past. It is evident from these studies that the surface pH can be 1–1.5 pH units lower than the 'effective' pH of the paper as determined from an aqueous extract (Saverwyns et al. 2002, Strlič et al. 2004, Reist 2006). Especially when dealing with papers loaded with alkaline fillers, the surface pH is 1–2 units lower compared to cold extraction pH (Bansa and Hofer 1984, Strlič et al. 2004, Blüher 2006). In addition to the systematic error of the surface pH method and the influence of CO₂ in the atmosphere, one must take into account the low solubility of alkaline earth carbonates (Kelly 1989, Strlič et al. 2004).

2.2 Alkaline reserve

The concentration of the alkaline reserve is the second important parameter for evaluating whether a deacidification treatment has been successful. The alkaline reserve is a deposit of alkaline earth carbonate or oxide within the paper matrix. It should protect paper against future degradation by acids and is effective until its neutralization capacity is exhausted. Ideally, it is deposited as evenly as possible during mass deacidification. According to the DIN recommendations and the Swiss Quality Standard, a treatment can be regarded as successful only if the concentration

of the alkaline reserve ranges between 0.06–0.24 mol/kg, that is 0.5–2% (w/w) expressed as magnesium carbonate (MgCO_3). The ISO 10716: 1994 standard serves as a standard procedure for determination the percentage of alkaline reserve deposited in paper; it is a destructive method and is also extremely time-consuming to perform. Instrumental techniques, such as X-ray fluorescence (XRF), which is non-destructive, and inductively coupled plasma optical emission spectrometry (ICP-OES), a destructive technique, can also determine the amount of alkaline reserve. In both cases it is an indirect approach based either on quantifying the element titanium (Ti) or magnesium (Mg). The non-destructive XRF technique is limited to processes that deposit magnesium carbonate and titanium oxide in the paper (Papersave⁷). It only is available through Nitrochemie Wimmis AG.

Quality standards and techniques for the determination of the alkaline reserve and their limitations will be discussed in greater detail in Part II of this study on sustainability in mass deacidification.

3. Selection of samples

Mass deacidification started already in 1994 at the German National Library in Leipzig (DNB) and in 1998 at the Berlin State Library (SBB). A considerable amount of books in both collections has already been treated. The previously treated books were selected randomly to obtain a manageable sample set for the project. The determination of a reasonable number of sample books is dependent on the standard deviation of parameters and the accuracy that should be obtained. From previous investigations concerning the efficiency of mass deacidification treatments, the standard deviations to be expected from the analytical techniques are known (Saverwyns et al. 2002, Ramin et al. 2009). The one with the lowest accuracy is surface pH determination, i.e. it shows the highest standard deviation. Therefore, the accuracy of surface pH analysis is the limiting factor and determines the number of sample books that is needed to gain data with a probability of 80% (Cochran 1972, Heinrich 2006, Luderer et al. 2008). Taking this into account, it was calculated that a set of 30 sample books would be enough to get satisfactory information. This figure was modified in so far as the number of selected sample books was adjusted according to the number of books that have been treated per year of deacidification campaign in the respective libraries. In conjunction with the sampling process, selected books were classified according to their state of preservation in the categories ‘good’, ‘medium’ and ‘bad’. A pH test using a pH pen was applied to check that the books had indeed been deacidified. A simplified scheme of the sampling process and the analytical techniques applied is given in Fig.1.

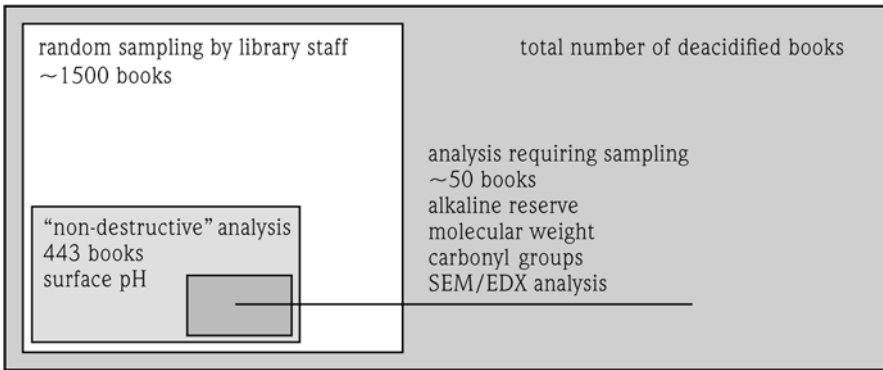


Fig. 1: Simplified scheme of random sampling from the stock of deacidified books.

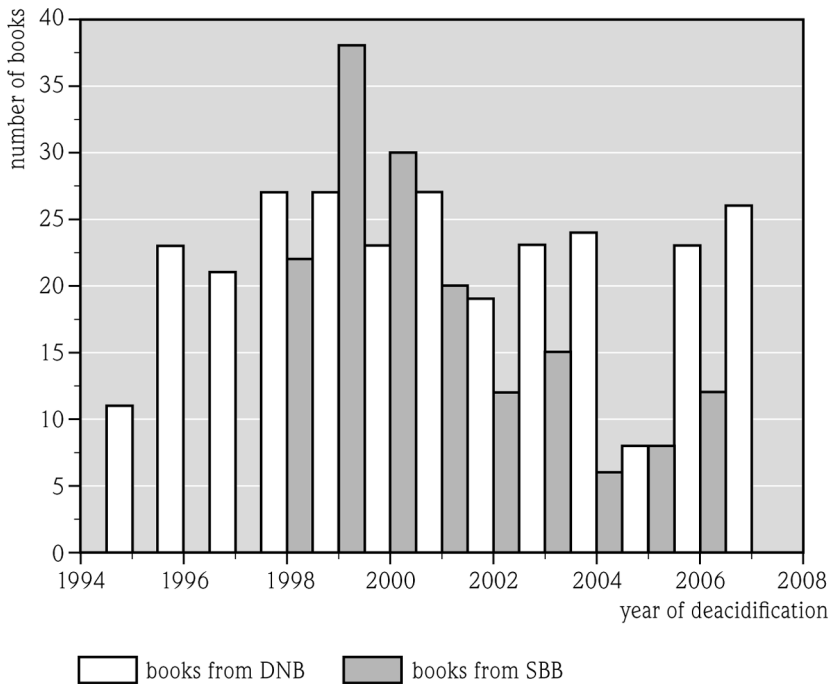


Fig. 2: Number of sample books plotted versus year of deacidification.

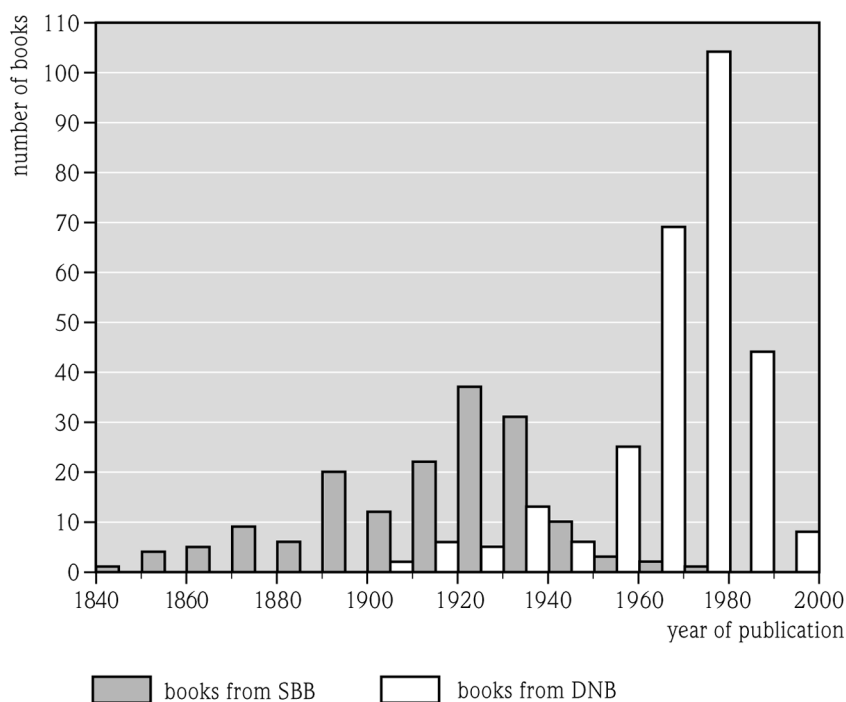


Fig. 3: Number of sample books analysed by year of publication.

The selected books varied widely with regard to their publication date. The DNB had mainly deacidified books dating from 1960 to 1980, while the SBB had treated books published between 1847 and 1998. From a purely visual inspection it was evident that the books from DNB were in much better condition. Only little discolouration of paper and far less mechanical damage were observed in comparison to samples selected from the SBB collection. In total, 282 books from the German National Library Leipzig (DNB) and 161 books from the Berlin State Library (SBB) were chosen for this study. All books had been subjected to deacidification by different processes, as described below, during the period from 1994 to 2006. A total number of 443 books were selected from both collections. The number of sample books with regard to the year of deacidification is given in Fig. 2, with regard to the year of publication in Fig. 3.

4. Methods and materials

4.1. Surface pH

Keeping in mind the limitations of surface pH measurements, this technique was used on all selected books, since it is still regarded as one of the most important criteria in quality control (Reist 2006, Gerlach 2006, Andres et al. 2008, Hofmann and Wiesner 2011).

All of the results are averaged values of two or four measurements. The 282 books selected from the collection of the German National Library (DNB) were measured at the conservation department of the DNB in Leipzig. The 161 books from the Berlin State Library (SBB) were measured at the Department of Chemistry of the University of Natural Resources and Life Sciences, Vienna (BOKU). Identical instruments, i.e. a Mettler Toledo SevenEasy pH meter and a flat combination pH electrode (Mettler Toledo InLab™ Surface, pH 1–11, 0–50°C) were used in both institutions. Calibration of the pH electrode was carried out according to the TAPPI method T529 om-99 using commercially available standard buffer solutions from Aldrich™. The measurements were performed with water of identical grade of purification that was provided by BOKU. First, two areas, one spot in the centre and one spot at the upper right margin of one page at the beginning of the book block and one page in the centre of the book were measured (Fig. 4). If the difference between centre and margin exceeded one pH unit, a second page from the centre of the book was measured in addition. Similar to the recommendations of Saverwyns et al. (2002) the measurement protocol was modified to improve its accuracy as follows:

- 100 µl of water was applied for a single measurement with an Eppendorf Reference® pipette,
- the pH reading was taken when the value had not changed for 10 seconds, allowing a maximum equilibrium time of 10 minutes.

However, it was not possible to limit the dimensions of the wetted paper area so that the ratio of paper and water remained improperly defined – a drawback of the method especially in case of highly absorbant papers.

4.2. Alkaline reserve

The amount of alkaline reserve was determined according to ISO 10716. Two grams of sample material are used; 1 g for quantification of the moisture content of paper samples according to ISO 287 (oven-drying method at 105°C) and 1 g to per

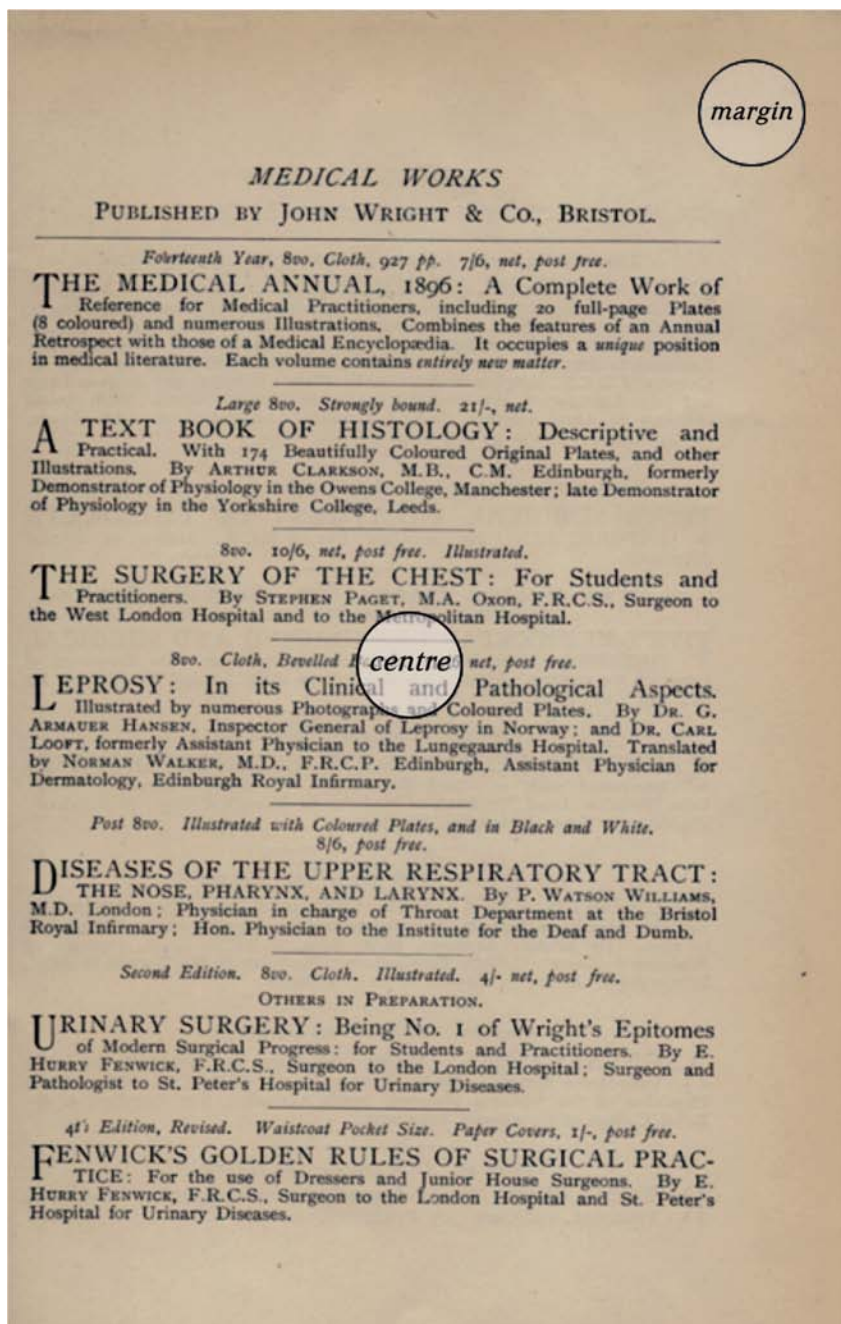


Fig. 4: Measurement areas on book pages for the determination of surface pH.

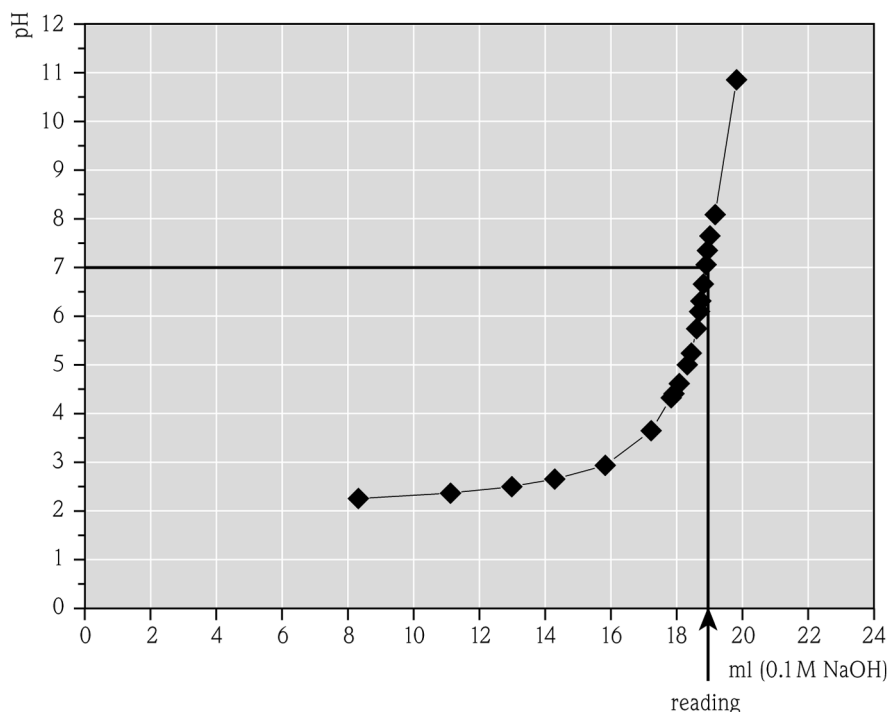


Fig. 5: Titration curve recorded to quantify alkaline reserve in deacidified book papers based on ISO 10716; end point taken at pH 7.

form analysis of the alkalinity of the paper by titration. For this purpose samples were cut roughly in 1 cm² pieces and boiled in 100 ml of purified water. Boiling was continued after addition of 20 ml 0.1 M hydrochloric acid that dissolves and neutralizes the alkaline earth carbonates. The excess hydrochloric acid was subsequently titrated with 0.1 M sodium hydroxide until pH 7 was reached. From the consumed volume of 0.1 M sodium hydroxide solution the total alkalinity, i.e. the alkaline reserve was calculated expressed as percentage (% w/w) of MgCO₃.

ISO 10716 suggests methyl red in ethanol for acidimetric titration. However, the colour change from red to yellow at the end-point could not be identified accurately because the solution was of a yellowish opaque colour caused by degradation products that were extracted from the paper sample. Therefore, a titration curve was recorded by means of a pH electrode that could accurately determine the end-point at pH 7 (Fig. 5).

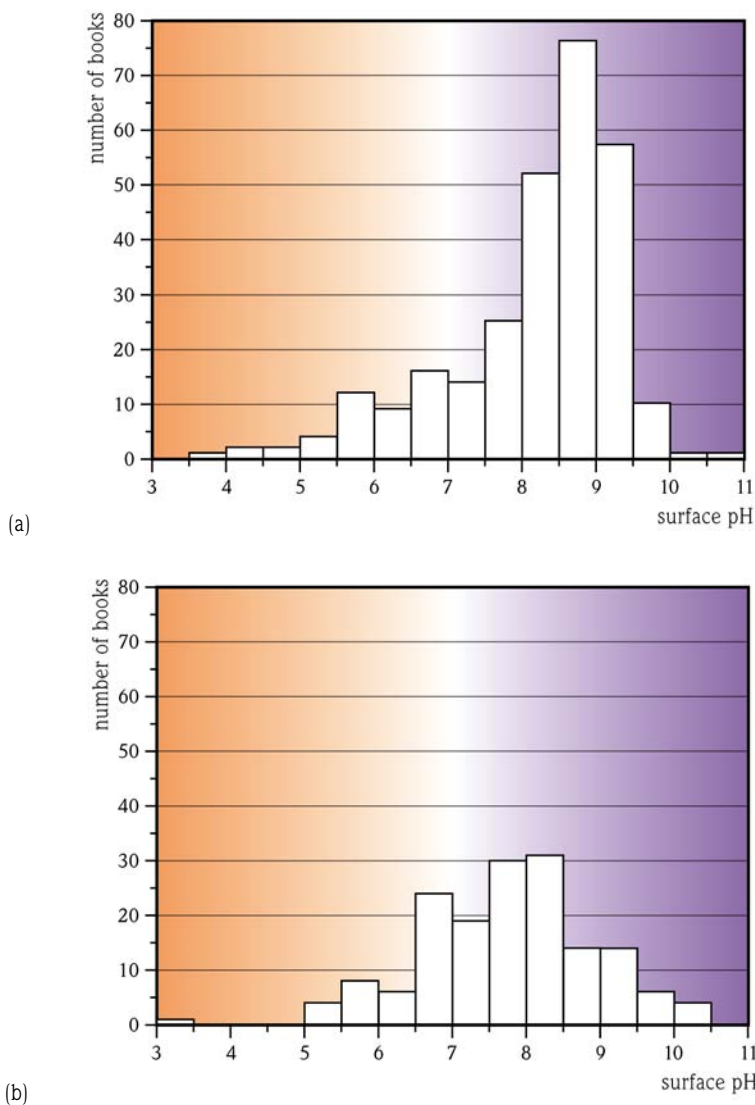


Fig. 6: Histograms of surface pH obtained in 2009 on sample books from DNB (a) and SBB (b).

5. Results and discussion

Figures 6 and 7 summarize the results of surface pH measurements obtained for all 443 sample books. Fig. 6. shows pH values of the sample books from DNB and Fig. 6b shows pH values of the SBB sample books. Only 84% of the samples from

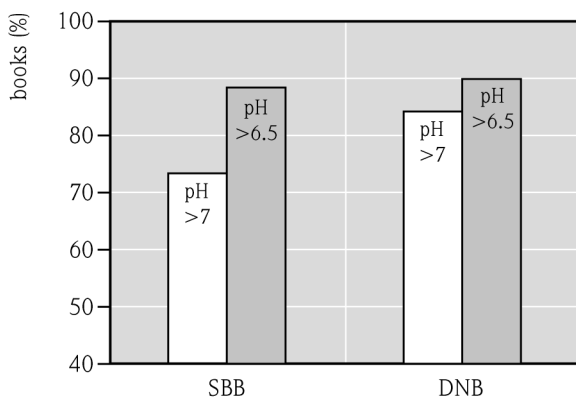


Fig. 7: Percentage of books (SBB left, DNB right) with surface pH > 6.5 and > 7. (Data from the 2005–2006 deacidification campaign and of samples treated with the Libartec™ process are not included)

the DNB and 73% of the samples from the SBB met a pH ≥ 7 (Fig. 7). However, according to the DIN recommendations a treatment can be regarded as successful only if papers feature a minimum surface pH of 7 across the sheet (Hofmann and Wiesner 2011, Andres et al. 2008, Großenbacher 2006). It is important to consider also that the surface pH of book papers after deacidification remains highly dependent on the material composition of the paper and its state of preservation at the time when subjected to deacidification. The influence of these parameters are difficult to judge, making it difficult to assess the data obtained. For the evaluation of the data set concerning a relation of surface pH with the year of publication of treated books, homogeneity of treatment, re-acidification, and the alkaline reserve deposited, it was of advantage that significant differences in surface pH in the sets of sample books from SBB and DNB existed.

5.1 Surface pH versus year of publication

The reason that among the samples from the SBB, a significantly smaller number fulfills the DIN recommendation for deacidified books with regard to their surface pH becomes evident in Fig. 8: Among books published from 1960 onwards, a higher percentage feature paper with a pH > 7 compared with book published before 1960. Generally, they are also in a poorer state of preservation. Hence, the treatment efficacy is lower for paper that is strongly preaged at the time of deacidification treatment.

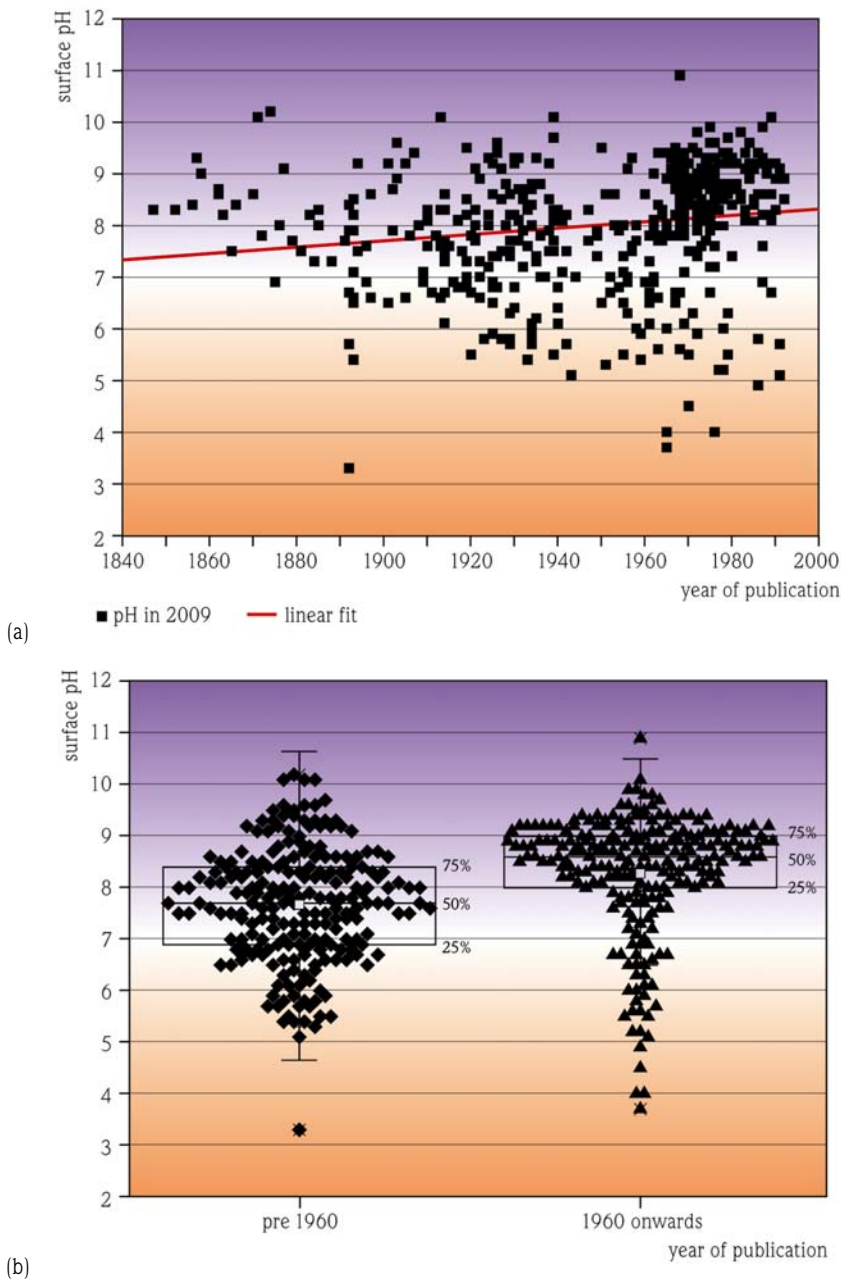


Fig. 8: Surface pH obtained in 2009 from all books vs. year of publication (a) and box plot of data according to their date of publication before 1960 (left) and after 1960 (right) (b).

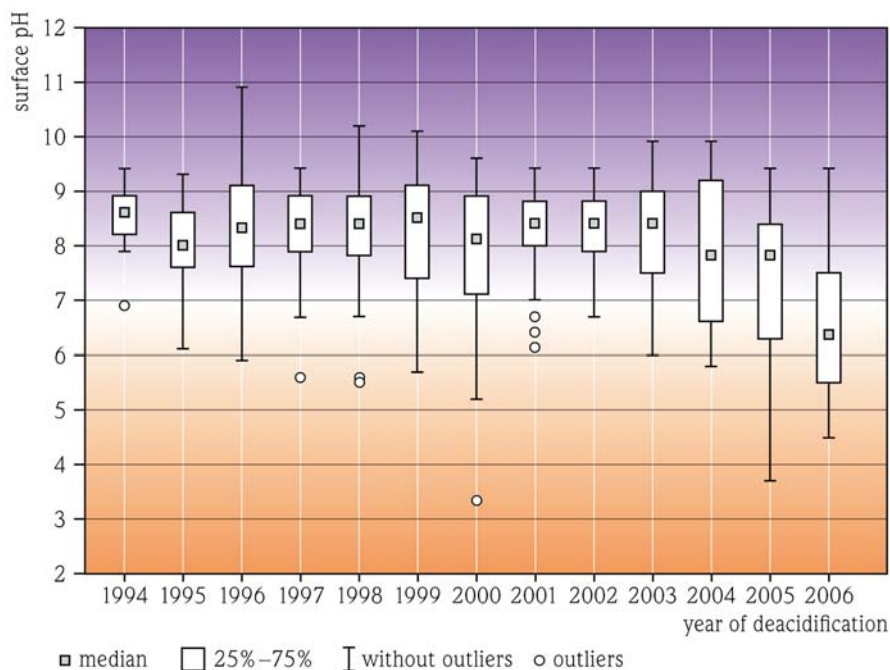


Fig. 9: Box plot of surface pH obtained in 2009 on all sample books vs. year of deacidification campaign.

Natural ageing of paper causes the formation of oxidized groups attached to the cellulose – mostly carbonyl groups. Through the creation of an alkaline environment by deacidification, they are transformed into additional carboxyl groups. These groups are, among other factors, responsible for a higher consumption of the deacidifying agent. This eventually results in a lower concentration of alkaline reserve deposited. In addition, the surface characteristics of paper are modified in the course of ageing in that its porosity is reduced while its hydrophobicity is increased. This phenomenon is the result of molecular changes in the cellulose structure, whose driving force are, at least partly, oxidative mechanisms. With regard to liquid phase deacidification processes, the penetration of the treatment solution is reduced, so that only limited treatment effectivity is to be expected.

5.2 Influence of the deacidification process on surface pH

No distinctive correlation between surface pH and the year of deacidification could be observed: pH data range mostly between 7 and 9 except for 2005 and 2006. To

Table 1: Result of Tukey HSD (Honestly Significant Difference) test of pH of each year of deacidification.

	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
1994		0.99	1.00	1.00	1.00	1.00	0.90	1.00	1.00	1.00	0.99	0.03	0.00
1995	0.99		1.00	1.00	0.99	1.00	1.00	1.00	1.00	1.00	1.00	0.24	0.00
1996	1.00	1.00		1.00	1.00	1.00	0.91	1.00	1.00	1.00	1.00	0.01	0.00
1997	1.00	1.00	1.00		1.00	1.00	0.88	1.00	1.00	1.00	1.00	0.00	0.00
1998	1.00	0.99	1.00	1.00		1.00	0.66	1.00	1.00	1.00	1.00	0.00	0.00
1999	1.00	1.00	1.00	1.00	1.00		0.74	1.00	1.00	1.00	1.00	0.00	0.00
2000	0.90	1.00	0.91	0.88	0.66	0.74		0.83	0.89	0.94	1.00	0.14	0.00
2001	1.00	1.00	1.00	1.00	1.00	1.00	0.83		1.00	1.00	1.00	0.00	0.00
2002	1.00	1.00	1.00	1.00	1.00	1.00	0.89	1.00		1.00	1.00	0.00	0.00
2003	1.00	1.00	1.00	1.00	1.00	1.00	0.94	1.00	1.00		1.00	0.00	0.00
2004	0.99	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00		0.57	0.01
2005	0.03	0.24	0.01	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.57		0.66
2006	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.66	

compare each year's data set statistically, a one way Analysis of Variance (ANOVA) was performed. Tukey's test was used for multiple pairwise comparisons of the means with Statistica 9.0 (Montgomery 2000, 96), and differences between data sets were tested at a probability level of $p < 0.05$. Except for 2005 and 2006, all data sets were similar without significant differences, which means they are all comparable (Fig. 9). The pH of papers deacidified in 2005 and 2006 (mean 7.2 and 6.6) was, however, significantly different from the other years of deacidification (mean 8–8.6 between 1994 and 2003, Fig. 9, Table 1). In terms of year of publication, books deacidified from 2005 to 2006 were not different from other sample books, and the books were of similar condition. Both libraries changed the deacidification process from Papersave™ to CSC Book Saver™ in 2004. As each company operating mass deacidification processes pursue their own quality standard, i.e. a target alkaline reserve, the choice of treatment process is the main factor for the lower pH in books treated in 2005 and 2006. Fig. 10 supports the process dependency of pH as the average surface pH achieved by the CSC Book Saver™ process of 7.0 was considerably lower and with larger deviations compared the Papersave™ process that achieved an average surface pH of 8.1.

The Libertec™ process produced in average a relatively high pH of 9.0 because it is supposed to leave an alkaline reserve on the paper surface. In this case, surface pH does not reflect the quality of the treatment properly. Since only 6.5 % of the books treated by Libertec were included in this study, the overall tendency by year of deacidification was not influenced.

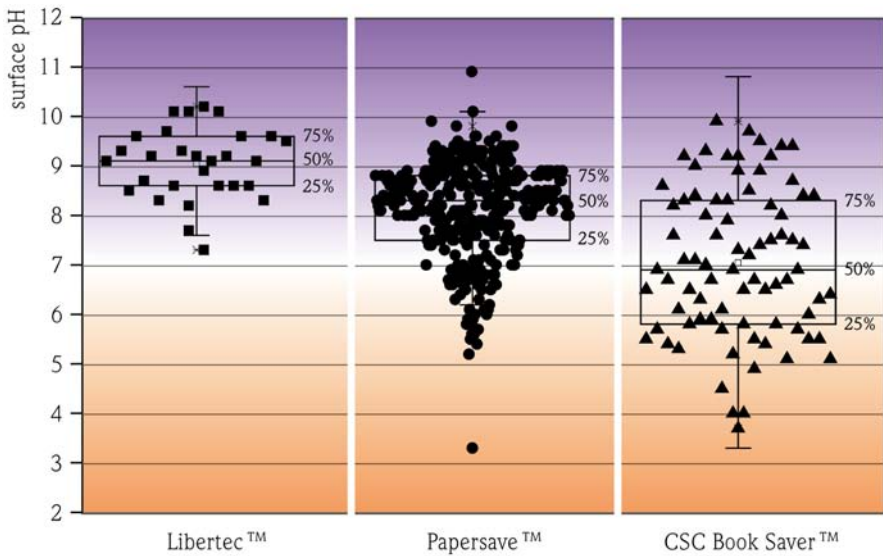


Fig. 10: Surface pH obtained in 2009 of all books given as box plots separated according to the deacidification process applied.

5.3 Homogeneity of surface pH across paper sheets and book blocks

The surface pH values obtained on the areas of papers indicated in Fig. 4 of those sample books treated with the Papersave™ process were comparable regardless from what collection sample books were taken (Figs. 11, 12a). However, the surface pH of the SBB samples treated with the CSC Book Saver™ process were less comparable and more varied (Fig. 12b). For statistical comparison of data measured on different locations the Kruskal-Wallis H-test as a non-parametric statistical test in which median and quantiles are used was applied because these data were not normally distributed (StatSoft, Inc., 2010). When data sets of the books treated with the Papersave™ process from both libraries were compared, there were no significant differences with a probability of 95 % among different areas measured. Consequently, it can be assumed that they had been treated homogeneously. However, in SBB sample books treated with the CSC Book Saver™ process, values obtained from either measuring pages at the beginning of book block or those obtained from pages of the middle of the book block feature marked fluctuations (Fig. 12b). From the statistical evaluation of the data it can be stated with a probability of 90 %, that

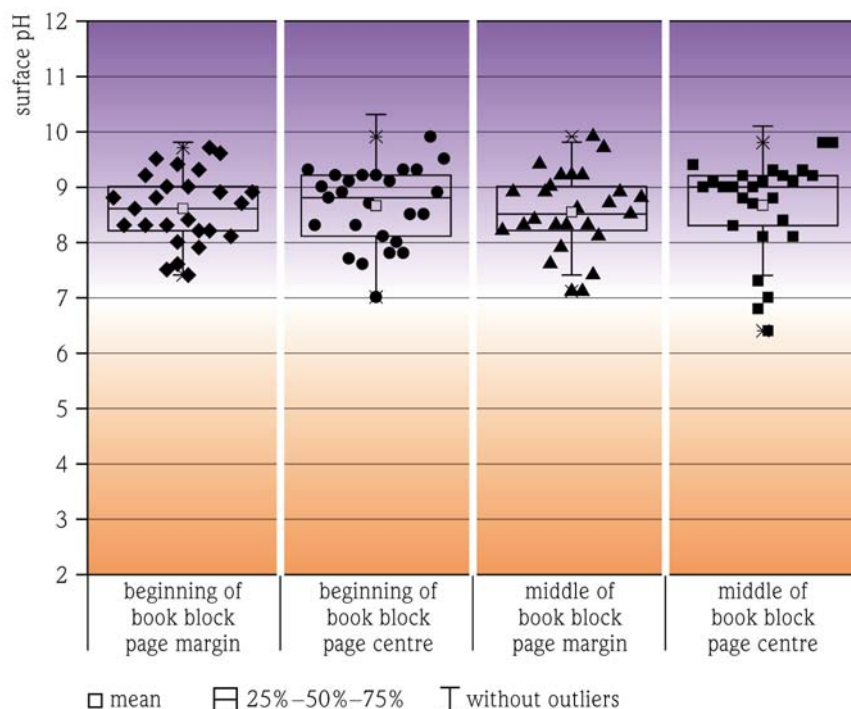


Fig. 11: Surface pH of obtained on DNB sample books in 2009; all books treated with the Paper-save™ process; 'beginning of book block' indicates page numbers 1 and 20; measurement areas 'margin' and 'centre' are indicated in Fig. 4.

treatments with the CSC Book Saver™ process lead to relatively inhomogeneous results.

5.4 Re-acidification of deacidified paper

Generally book paper becomes more acidic in the course of time. Alum-rosin sizing is known to induce significant acid formation. Atmospheric pollutants such as sulphur dioxide or nitrogen dioxide contribute to an increase in paper acidity especially in margin areas (Bégin et al. 1999, Havermans and Steemers 2005). In addition, organic acids can be generated as a result of cellulose degradation in paper. Volatile acidic compounds, e.g. acetic acid and formic acids are known oxidative degradation products of lignocellulosic materials (Banik et al. 2006, Strlič et al. 2007); the emis-

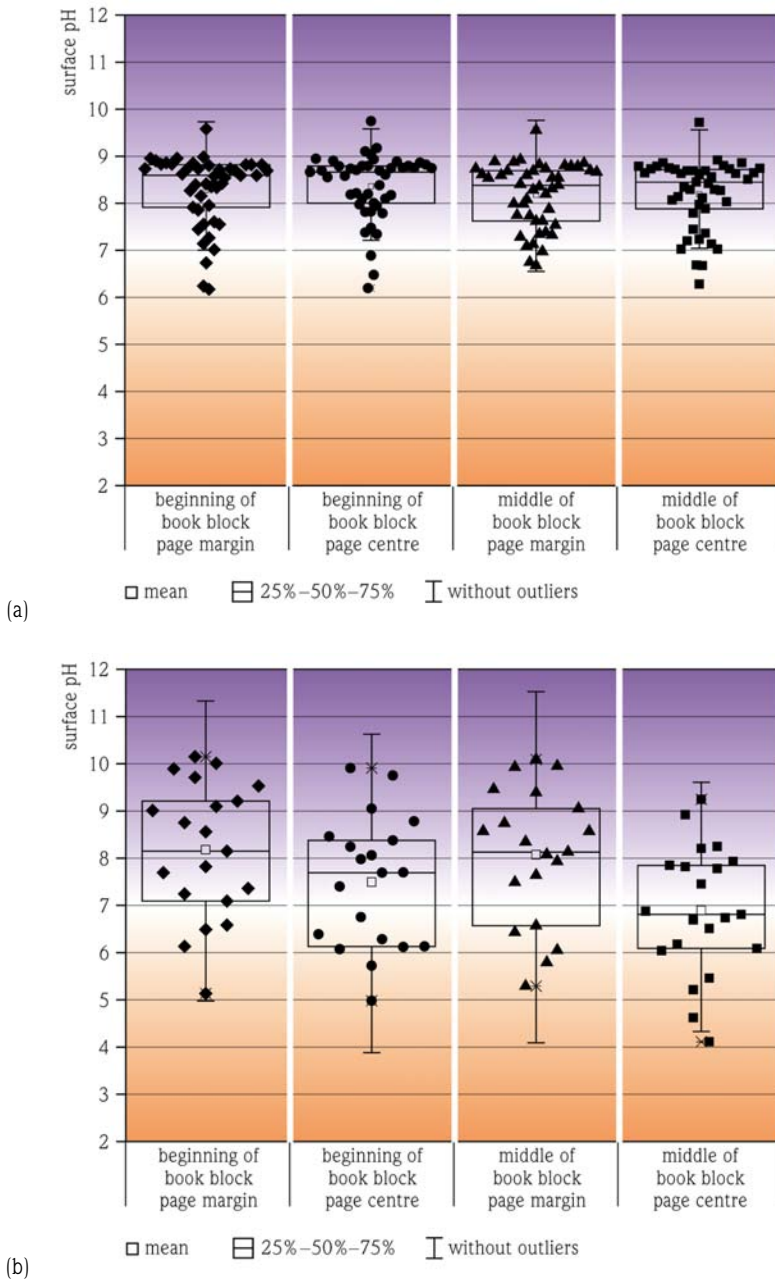


Fig. 11: Surface pH obtained on sample books from SBB right after deacidification; a: treated with the Papersave™ process; b: treated with the CSC Book Saver™ process.

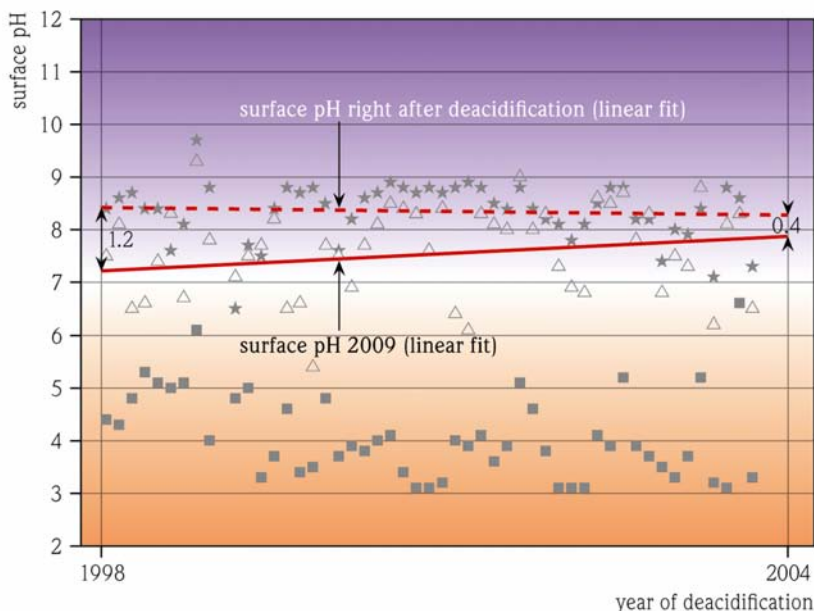


Fig. 13: Surface pH of sample books before deacidification (square), right after deacidification (star) and data obtained of the same books in 2009 (triangle) plotted vs. year of deacidification. Only data from Papersave™ process are considered. The pH before deacidification and right after deacidification measured by staff members of SBB according to the non-refined TAPPI T529 method.

sion of other carboxylic acids such as octanoic and decanoic acids from naturally aged groundwood paper was also reported (Lattuati-Derieux et al. 2004, Pedersoli Jr. et al. 2011). Photochemical oxidation of lignin and hemicellulose can cause the increase of carboxylic groups in the molecular structure which consequently lowers the pH of paper (Carter 1989). The re-acidification of deacidified paper during accelerated ageing has been shown in many articles (Bansa 1998, Blüher 2006, Ramin et al. 2009, Hanus et al. 2006). Hence, the extent of re-acidification depends not only on the amount of alkaline reserve deposited, but also on a number of other factors like paper type and quality. Therefore, re-acidification is difficult to predict. The formation of volatile acids in deacidified paper has also been observed, yet the quantity is lower than in non-deacidified papers (Shahani et al. 2001, Doering 2007), i.e. a certain amount of alkaline reserve in deacidified paper will be consumed for neutralisation of acids which are generated over time.

To get insight into the re-acidification of deacidified book papers it is necessary to include data of pH measurements obtained during a longer period. Fortunately, the

SBB provided respective data of 51 of the 161 sample books, of which the surface pH before and right after deacidification has been measured. All sample books were deacidified by the Papersave™ process. In Fig. 13 the data of surface pH measurements right after the deacidification that took place between 1998 and 2004 are presented in comparison with those obtained on the same books in 2009. The longer ago the deacidification was, the lower were the pH values obtained in 2009. Comparing average data gained right after deacidification in 1998 to data measured 2009 (11 years later), the surface pH is about 1.2 units lower. Although the absolute data are not comparable because of differences in the instrumentation, the analytical procedure and electrode calibration, as well as operator variation that must be taken into account, we can conclude that the paper has re-acidified to some extent.

5.5 Relation of the surface pH to the alkaline reserve

Fig. 14 shows a plot of % alkaline reserve determined by titration (DIN ISO 10716) versus surface pH measured in the centre of the same paper used for determination of the alkaline reserve. In an alkaline environment above pH 7.6 (A region in Fig. 14) there is no reasonable correlation between surface pH and alkaline reserve due to the low solubility of alkaline earth carbonates deposited in the paper. Therefore, pH cannot be considered a meaningful parameter when the determination of alkaline reserve after mass deacidification is required. This has already been stated by Saveryns et al. in 2002.

However, in the acidic areas below pH 5.1 (see B region in Fig. 14), a good correlation between acidity – expressed here as negative alkaline reserve – and surface pH can be found. Additionally, there is a weak correlation between a low amount of alkaline reserve (~ 0–0.3 % MgCO_3) and a surface pH from 5.1 to 7.6 in the middle region between A and B in Fig. 14.

The surface pH must not be used as a single parameter to evaluate the success of deacidification. Its significance however is sufficient for the detection of incomplete deacidification treatments. Near pH 7, which constitutes the lower threshold pH for quality control in mass deacidification, a successful deacidification is not always guaranteed in terms of sustainability since pH 7 often corresponds with a low amount of alkaline reserve. This gives a new perspective on the ongoing debate whether neutral (pH 7) or slightly acid (pH 6.5) surface pH of paper after mass deacidification is an acceptable treatment result. From the present results, neutral and slightly acid surface pH of paper cannot be regarded as sustainable results because it tends to correlate with a too low alkaline reserve.

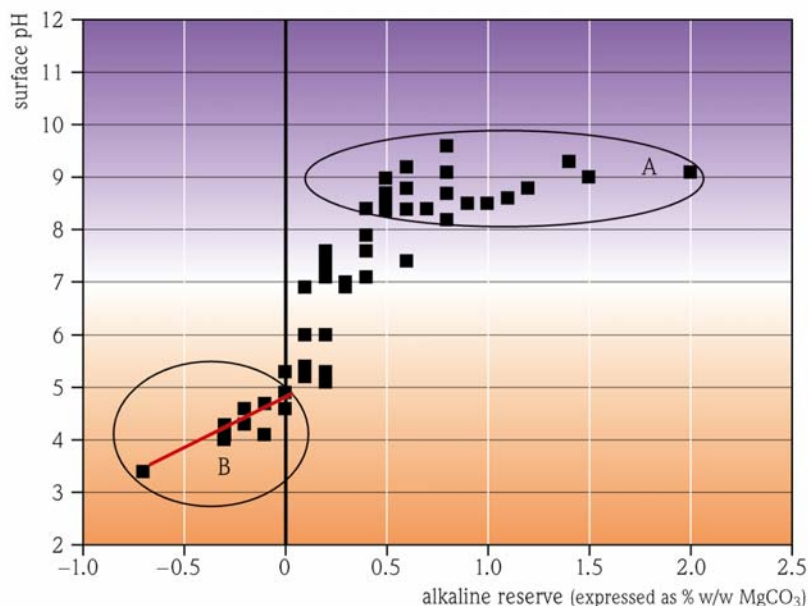


Fig. 14: Plot of alkaline reserve (% w/w MgCO₃) determined by titration vs. surface pH data obtained on the same page. Region A: High alkaline reserve, region B: Negative alkaline reserve which shows correlation to pH.

Further, measuring surface pH is very valuable for non-deacidified books, since a good linear correlation to the acidity is evident (Fig. 14 B region), which can either be used to predict how much overall alkali deposit will be needed to accomplish a full neutralisation of acids or to identify books with insufficient deposition of alkaline reserve after mass deacidification.

6. Conclusions

Surface pH measurements were carried out on papers of 443 books selected from the collections of two main German libraries. The books have been subjected to mass deacidification during the period from 1994 to 2006. Data obtained of about 80% of the analyzed book papers showed that a pH of ≥ 7 was met through deacidification. Several conclusions can be drawn from this study:

1. The amount of alkaline reserve depends on the process used. This can be seen retrospectively in the study of previously deacidified samples. For mass deacidifica-

tion realized during the period from 1996 to 2003 a rather homogeneous surface pH of about 8 to 8.6 was observed, while samples that were treated in 2005 and 2006 featured a lower surface pH (7.2 and 6.6). This is mainly to be attributed to a change in the deacidification process that was applied from 2004 onwards in both libraries.

2. Books that are already in a poor state of preservation at the time of treatment will have a lower and a less homogeneous pH after treatment within a given sample set. It can be concluded that the treatment depends on the condition of the paper. Deacidification is apparently less beneficial and controllable for significantly deteriorated paper.

3. Previously deacidified book papers shows a noticeable degree of re-acidification over a period of 10 years examined in this study. This was shown by the comparison of surface pH values.

4. The technique of surface pH measurement by itself is not sufficiently accurate to evaluate the degree of re-acidification. This only can be determined by analysing the residual alkalinity present in paper. A suitable system enabling libraries to evaluate these important data is still lacking. This study confirms the conclusion of other authors who have stated that surface pH does not allow the estimation of the alkaline reserve deposited in paper as result of a mass deacidification.

5. However, it could be shown that the surface pH around pH 7 can be used to indicate a low amount of alkaline reserve that generally does not meet the quality requirements defining the amount of alkaline reserve that must be deposited in paper by mass deacidification. Therefore, surface pH provides valuable information if used as a simple and low-cost technique to check the quality of mass deacidification interventions.

6. Measuring the surface pH of yet untreated paper is useful because it provides a rough estimate of the amount of alkali needed for its complete deacidification during mass deacidification treatment.

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Zusammenfassung

Nachhaltigkeit der Massenentsäuerung von Bibliotheksgut. Teil I:

Untersuchungskonzept, statistische Probennahme und Bestimmung des Oberflächen pH.

Die Deutsche Nationalbibliothek (DNB) und die Staatsbibliothek zu Berlin – Preußischer Kulturbesitz (SBB) haben seit 1994, bzw. seit 1998 Teile ihrer Bestände einer Entsäuerung unterzogen, wobei die Verfahren von Papersave®, Libertec® und CSC–Book Saver® Anwendung fanden. Die Nachhaltigkeit der jeweiligen Prozesse wurde an Originalbüchern der beiden teilnehmenden Bibliotheken wissenschaftlich überprüft. Dazu wurden insgesamt 443 Bücher herangezogen, die bis 2006 entsäuert worden waren. Die Untersuchungen umfassten die Bestimmung des Oberflächen-pH und der alkalische Reserve, sowie die Analyse der mittleren Molmasse und des Oxidationsgrades der Cellulose mittels Gelpermeationschromatographie (GPC). In Teil 1 der Studie werden zunächst die Probenahme sowie die Resultate der Oberflächen-pH-Messungen vorgestellt. Ein Oberflächen-pH unterhalb 7 kann mit dem Säuregehalt von Papier korreliert werden und somit als Indikator für den Grad der Versäuerung dienen. Es zeigte sich, dass die Papiere von 80% der behandelten Bücher im Jahr 2009 einen Oberflächen-pH von ≈ 7 aufwiesen. Im Allgemeinen unterschieden sich die erhobenen Werte nicht in Abhängigkeit vom Jahr der Entsäuerung; für die Jahre 2005 und 2006 wurden allerdings signifikant geringere pH-Werte gefunden. Weiterhin zeigte sich bei einem Vergleich der Daten aktueller pH-Bestimmungen mit denen unmittelbar nach der Entsäuerung ein abfallender Trend, der auf eine leichte Rücksäuerung des Papiers im Zuge der natürlichen Alterung hinweist. Diese Beobachtung trifft besonders auf Bücher mit einem älteren Publikationsdatum zu. Hier streuten die Messdaten auch stärker.

Résumé

Efficacité à long terme de la désacidification de masse des objets de bibliothèques.

Partie I: concept d'étude, échantillonnage statistique et détermination du pH de surface.

La Bibliothèque nationale allemande (BNA) et la Bibliothèque d'Etat de Berlin – propriété de la Fondation du Patrimoine culturel prussien (BEB) ont désacidifié une partie de leurs fonds, depuis 1994 pour la BNA et 1998 pour la BEB. Elles ont utilisé les procédés de papersave®, de Libertec® et de CSC-Booksaver®. L'efficacité à long terme de chaque procédé a été contrôlée scientifiquement sur des livres originaux des deux bibliothèques. Au total, 443 livres ont été traités jusqu'en 2006. Les tests ont mesuré le pH de surface et la réserve alcaline, et analysé le poids moléculaire moyen et le degré d'oxydation de la cellulose par la méthode de chromatographie par filtration sur gel. La première partie de l'étude présente les échantillonnages et les résultats des mesures du pH de surface.

Un pH de surface inférieur à 7 peut être mis en corrélation avec la teneur en acide du papier et servir d'indicateur de l'acidité. Il s'est avéré que le papier de 80 % des livres traités en 2009 avaient un pH de surface inférieur à 7. Dans l'ensemble, les valeurs obtenues ne dépendent pas de l'année de la désacidification, puisque des valeurs pH bien moindres ont été trouvées pour 2005 et 2006. De plus, une comparaison des données des mesures actuelles du pH avec les valeurs mesurées immédiatement après la désacidification a montré une tendance à la baisse, qui indique une légère ré-acidification du papier au cours du vieillissement naturel. Cette observation se vérifie notamment pour les livres publiés il y a plus longtemps. Dans ce cas, les valeurs sont encore plus éparées.

Authors and contacts

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Ute Henniges gained a PhD in 2008 at the University of Natural Resources and Life Sciences, Vienna (BOKU Wien) and is a trained paper conservator. From 1999–2003 she studied conservation of paper based cultural heritage at the Academy of Art and Design in Stuttgart. In 2002/2003 she received a grant of the Landesstiftung Baden-Württemberg that she spent at the Universitat Politècnica de Catalunya in Terrassa (Spain). From 2003 to 2005 she was employed at PAL Preservation Academy GmbH Leipzig as paper conservator.

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Paper II

**Sustainability of mass
deacidification-Part II:
Evaluation of alkaline
reserve**

Restaurator, vol. 33, pp. 48-75.

Sustainability of Mass-Deacidification. Part II: Evaluation of Alkaline Reserve

by Kyujin Ahn, Gerhard Banik and Antje Potthast

Abstract: Alkaline reserve can be considered as a parameter of utmost importance in mass deacidification. The amount of alkaline reserve in paper introduced by the respective process determines the overall success of mass deacidification to a large extent. Alkaline reserve is also of particular interest for understanding the long term effectiveness of mass deacidification. In this paper, we present the results of evaluating alkaline reserve in books deacidified between 1994 and 2006 in two large German libraries, the German National Library (DNB) in Leipzig and the Berlin State Library (SBB). Unfortunately, alkaline reserve in papers is a parameter which is not easily determined by chemical tests; hence we have compared different methods such as standard titration to evaluate the total amount of alkali reserve, XRF for the distribution of magnesium ions across the paper sheet and SEM-EDX to judge penetration into the paper matrix. The laborious titration technique is so far the only reliable method to determine the amount of alkaline reserve in “real world” library material. In addition, the alkaline reserve measured in library books has been compared to the integrity of the cellulose after accelerated ageing by determining molecular weight distribution, an important tool to estimate the long-term stability of cellulose. The present study showed that only 52 % of the books analysed had an alkaline reserve fulfilling the lowest requirement of 0.5 % magnesium carbonate according to the DIN recommendations. The deacidification process and the age of the books were identified as the main factors influencing the amount of alkaline reserve. The CSC Book Saver™ process and the Papersave™ process resulted in an even distribution of fine magnesium ions over the paper surface, whereas the Libertec™ treated papers showed unevenly distributed, coarse particles. The most efficient deposit alkaline reserve within the paper matrix found in papers treated with the Papersave™ process. Comparisons of alkaline reserve with extensive cellulose analysis before and after accelerated ageing showed a direct relationship between the amount of alkaline reserve and cellulose degradation. Based on these results, a higher amount of alkaline reserve (0.8-1 % magnesium carbonate) than previously suggested as minimum requirement will be proposed in order to further improve the effectiveness of mass deacidification.

Zusammenfassung/résumé at end of article

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1. Introduction

As explained in our previous paper, scientific evaluation of books deacidified in the German National Library in Leipzig and the Berlin State Library from 1994 to 2006 started in 2008 (Ahn et al. 2011). The overall quality of the treatment was initially

assessed by surface pH measurements. 80 % of the books were successfully treated, reaching pH 7 or higher. A clear tendency for reacidification was observed. As a second part of the study, alkaline reserve – being an important parameter for long term quality of mass deacidification – was determined. The relationship of alkaline reserve and long term stability of cellulose was addressed in particular. This paper will mainly discuss the role of alkaline reserve in deacidified books which will be evaluated according to various criteria, emphasizing the importance of improving efficiency of deacidification treatments in respect to cellulose stability. Alkaline reserve was determined using XRF as well as the standard titration method. It will also be shown that homogeneity of distribution within a single paper sheet has to be considered an important quality control parameter. Alkaline reserve deposits on the surface and the cross-sectioned area of papers treated by three processes was examined by SEM-EDX in order to investigate its distribution throughout the paper matrix as well as surface. Changes of average molar mass (M_w) before and after accelerated ageing were determined using GPC (Gel permeation chromatography) analysis. GPC is a rather sensitive tool to address cellulose integrity as a major parameter of paper stability and turned out to be very valuable for judging the required amounts of alkaline reserve necessary to perform an optimized deacidification treatment.

1.1 Standards for determination of the alkaline reserve

The role of alkaline reserve relating to long-term paper stability was addressed by Hanson (1939) as early as 1930's and was based on observations of historic rag papers in good condition which contained 2 % of calcium carbonate at least. ISO 9706: 1994 and ISO 11108: 1996 which are the international standards for paper permanence define a minimum amount of alkaline reserve as an amount corresponding to 0.4 mol/kg of acid that is equal to 0.2 mol/kg of alkaline earth carbonates and 2 % of calcium carbonate. Other standards such as ANSI (American National Standards Institute) Z39.48: 1992 and DIN (Deutsches Institut für Normung) 6738: 2007-03 require the same amount of alkaline reserve. Although this requirement has been widely accepted, very few scientific studies have been carried out to support Hanson's observations and to determine specific quantities of alkaline reserve necessary to enhance permanence of all different types of papers.

As mass deacidification is intended to deposit a certain amount of alkaline reserve in the paper, alkaline reserve has always been an important parameter in quality control of mass deacidification. According to current recommendations of the quality by DIN, 0.06–0.24 mol/kg (0.5–2 % $MgCO_3$) of alkaline reserve are required for

the process control (Hofmann and Wiesner 2011). The values are lower than specified by standards for permanence in order to avoid negative effects of high alkaline deposits such as stiffness or brittleness of vulnerable paper (Hofmann and Wiesner 2011, Smith 2011). In addition, these lower concentrations of alkaline deposits avoid the well-known alkaline induced degradation of cellulose since book papers normally contain oxidized cellulose units which can cause β -elimination in alkaline conditions (Kolar and Novak 1996, Malesič et al. 2002). However, a recent study showed that oxidized papers can be resistant to alkaline damage given the deacidification treatment is not carried out at too high a pH, e.g. above pH 10 in case of an aqueous treatment (Stephens et al. 2009). Our results on this issue will be published elsewhere. In fact, the Library of Congress, Washington, uses a non-aqueous liquid suspension system (BookkeeperTM) and follows higher standard amounts of alkaline reserve than current DIN recommendations, specifying 1–3 % of alkaline reserve (LOC 2011). Libraries in Germany generally employ more moderate treatments, considering current DIN recommendations as their quality standard for alkaline reserve. The Swiss National Library (SNL) together with their service provider Nitrochemie Wimmis AG (NCW) implement similar standards as in Germany which are more precisely defined: 0.5–2 % MgCO_3 for test papers and 0.3–2.3 % MgCO_3 for original papers are required; a deacidification treatment is considered successful when at least 95 % of tested papers are within this range (Nitrochemie Wimmis AG 2004, Reist 2006, Blüher 2006, Andres et al. 2008).

Our results from alkaline reserve measurements will be discussed on the basis of the existing standards, e.g. the current DIN recommendations and the Swiss quality standard that is an internal standard of NCW and SNL.

1.2 Determination of alkaline reserve

ISO 10716: 1994 generally serves as a standard procedure for determination of % alkaline reserve that is required by the standards mentioned above. At least 3 g of sample material has to be destroyed for a single measurement; 2 g for the determination of moisture content according to ISO 287: 1985 and 1 g for titration of alkaline reserve according to ISO 10716: 1994. 1 g of paper can be half a page or even an entire page depending on the size of the book. In addition to the large amount of sample material required, the titration method is time consuming and laborious. ISO 10716: 1994 is certainly applicable for small numbers of samples, but when it comes to a mass process which also requires the analysis of a large number of samples in order to get statistically significant data, ISO 10716: 1994 cannot be con-

sidered as the method of choice. When assessing the homogeneity of a mass-deacidification process within one page, a method requiring less sample material is necessary. Clearly, there is a need for novel techniques which ideally should be fast and non-destructive. Due to disadvantages of the titration method, a variety of instrumental techniques for determination of alkaline reserve have been tested. A quantification of alkaline reserve based on a carbonate band of the paper's IR spectrum using IR DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) or ATR-FT IR (Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy) was investigated (Hilder 2010, Gibert Vives 2004). The method seems to be rather applicable to a high content (higher than the quality standard range) of alkaline earth carbonates in paper. In addition, the technique detects only alkaline deposits at the surface, which will lead to distortions when comparing processes, some of which deposit the alkaline reserve at the surface only, e.g. LibertecTM.

Another method for the determination of alkaline reserve was developed for the quality control of the Papersave SwissTM process conducted by NCW AG, Switzerland. X-ray fluorescence spectroscopy (XRF) was used to quantify the Mg content of treated paper with an internal standard Ti content (Blüher and Vogelsanger 2001, Andres et al. 2008). The method is non-destructive and fast. However, this technique has two drawbacks when the overall value of alkaline reserve is required: Firstly, the method is limited to papers treated by the PapersaveTM process, which uses a complex of magnesium-titanium ethoxide as the active agent. Due to a limitation of X-ray emission from light elements in a paper sheet, only the content of titanium can be directly quantified (atomic number of Ti = 22; atomic number of Mg = 12) using XRF. Secondly, this technique gives information only about the uptake of alkaline reserve, not the actual magnesium carbonate left in the paper which is typically lower because a certain amount of the deacidifying agent is consumed by the acidic components in the paper. Hence, XRF provides a fast evaluation of the distribution of Mg constituents across the sheet, which is also an important parameter for process control. However, for non-standardized library books, the value obtained does not reflect the actual alkaline reserve. In order to solve this problem, NCW calibrates % of MgCO₃ deducting the average acid content of the reference papers (-0.3 % of MgCO₃) (Andres et al. 2008). However, the measurement is still based on the assumptions that real book papers do not originally contain titanium and that variations of their acid content before deacidification are negligible.

On the other hand, elemental analysis techniques are a suitable tool for the evaluation of homogeneity of the treatment within a single page. The magnesium content can easily be determined on several spots, since these methods require none or a few hundred milligrams of sample material per measurement. For example,

ICP-OES is one of the methods proposed by DIN for the evaluation of homogeneity of alkaline reserve (Hofmann & Wiesner 2011).

Although homogeneity of mass deacidification is often considered as one of the quality control criteria, the standard leaves space for improvement: Only NCW and their library customers regulate it by standard deviation. At least 95 % of tested books should have standard deviations lower than 0.5 on a single page based on 6–7 measurements per page (Blüher 2006, Reist 2006, Andres et al. 2008).

Due to limited time and sample number of our study, XRF analysis of Mg constituents was adapted to the PapersaveTM treated books for the determination of alkaline reserve as well as for homogeneity of the treatment within one book page in addition to the standard titration method.

2. Materials and methods

2.1 Alkaline reserve by titration

Only a limited numbers of books could be used for titration, as this method requires extensive sampling. A selected number of deacidified sample books was twenty two. Additionally, seven non-deacidified duplicates were obtained from the antique markets in order to measure the acid content before deacidification. Sample books were published from 1892 to 1992 and were deacidified between 1994 and 2006. 10 books had been treated by the CSC Book SaverTM process operated by PAL, Preservation Academy Leipzig, 11 books had been treated by the PapersaveTM process operated by ZFB (Zentrum für Bucherhaltung), and one book had been deacidified by the LibertecTM process.

The amount of alkaline reserve was determined according to modified ISO 10716: 1994. 2 g of sample material are used; 1g for quantification of the moisture content of paper samples according to ISO 287: 1985 and 1 g to perform analysis of alkalinity of paper by titration. For this purpose samples are cut roughly in 100 mm² pieces and boiled in 100 ml of purified water. Boiling is continued after addition of 20 ml 0.1 M hydrochloric acid that dissolves and neutralises the alkaline earth carbonates. The excess hydrochloric acid is subsequently titrated with 0.1 M sodium hydroxide until pH 7 is reached. From the consumed volume of 0.1 M sodium hydroxide solution the total alkalinity, i.e. the alkaline reserve is calculated expressed as percentage (% w/w) of MgCO₃.

ISO 10716: 1994 suggests methyl red in ethanol for acidimetric titration. However, the colour change from red to yellow at the end-point could not be identified accurately because the solution featured as yellowish opaque colour caused by deg-

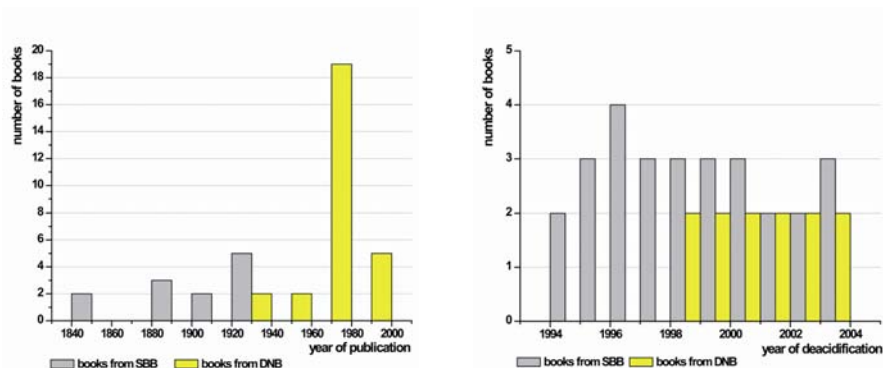


Fig. 1: Histogram of sample books for the determination of % MgCO_3 by XRF arranged by year of publication and histogram of sample books arranged by year of deacidification.

radation products that have been extracted from paper. Therefore, a titration curve was recorded by means of a pH electrode that could accurately determine the end-point at pH 7 as shown in the previous article, part 1 (Ahn et al. 2011).

2.2 Alkaline reserve by Mg constituent determined by XRF

Twenty eight books from the German National Library in Leipzig (DNB) and twelve books from the Berlin State Library (SBB) were chosen and analysed using XRF. As explained in the introduction, only books treated by the Papersave™ process could be included. The year of publication and the year of deacidification of each book can be seen in Fig. 1.

XRF analysis was performed by NCW AG, Switzerland, and the method was validated according to SN EN 45001 (Blüher and Vogelsanger 2001). Ti contents on 6–7 spots of the middle page of each book were measured and then the relative amount of Mg and % w/w of MgCO_3 was determined according to uptake ratio of Ti and Mg and the calibration to the known amounts of % w/w of MgCO_3 respectively. Thus the values presented in this paper are average values of 6–7 measurements. Ti was measured with following parameters: tube voltage 10 kV, tube current 0.2 mA, filter cellulose, livetime 50 sec, max. energy 10 keV. Each measurement covered an area of 150 mm^2 . In order to distinguish between data achieved by XRF analysis and data achieved by titration method, the percentage (% w/w) of MgCO_3 determined by XRF analysis will be expressed as % MgCO_3 (XRF).

2.3 Alkaline reserve by SEM-EDX

Three books treated by LibertecTM, PapersaveTM, and CSC Book SaverTM were selected to determine the alkaline reserve on the surface and within the paper matrix using SEM-EDX. Duplicates of the three books were included as non-treated references. The following books were chosen: LibertecTM treated: published in 1913 and deacidified in 1998. 0.3 % of MgCO₃/surface pH 9.3, PapersaveTM treated: published in 1968 and treated in 1998. 1.2 % of MgCO₃/surface pH 8.4, CSC Book SaverTM treated: published in 1988 and treated in 2005. 0.7 % of MgCO₃/surface pH 8.8. Au coating was applied to all samples for 60 seconds, and 30 kV of accelerating voltage was used on a Hitachi S-4000 device.

2.4 Determination of Mw and accelerated ageing protocol

Sample preparation for GPC analysis was carried out according to literature (Röhring et al. 2002), but in semi-micro scale, using half the sample amount and reagent compared to the standard method.

2.4.1 Mw General protocol

About 100 mg of each sample were disintegrated in water using a mixer. After removing excess water, 25 mg of the wet sample was taken and labeled with 2 ml of CCOA (carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy] amide) solution (1.25 g/L) in 20 mM zinc acetate buffer pH 4.0 for 7 days at 40 °C. Standard pulps were labeled in the same way. Excess CCOA was removed by filtration and the sample was washed with water and ethanol. The sample was then activated in pure DMAc for 24h. Finally, excess DMAc was removed and the DMAc-wet sample was dissolved in 1 ml of DMAc/LiCl 9 % (w/v). Samples were diluted three times with DMAc and filtered through a 0.45 µm filter prior to injection. This sample preparation was to produce the carbonyl group contents together with Mw. However, only Mw data will be introduced in this paper.

GPC conditions: The GPC system used for this project consists of two detectors; a multiple-angle laser light scattering detector (MALLS) (Wyatt Dawn DSP with argon ion laser ($\lambda_0=488\text{nm}$), and refractive index (RI) (Shodex RI-71). Four serial GPC columns were PL gel mixed ALS, 20µm, 7.5 x 300 mm. Degasser (Dionex DG-2410), autosampler (HP 1100), pulse damper pump, pump (Kontron 420), and column oven (Gynkotek STH 585) were also part of the system.

Table 1: Sample list and results of alkaline reserve (AR, % w/w MgCO_3) measurement by titration (ISO 10716)

No.	Year of deacidification	Year of publication	Process	% AR	% AR of non-deacidified duplicate	% AR by XRF [*]
1	1994	1986	Papersave TM	2.0	0.0	
2	1994	1992	Papersave TM	0.8	-0.1	1.25
3	1996	1960	Papersave TM	0.8		1.16
4	1997	1963	Papersave TM	1.4	-0.2	1.81
5	1998	1892	Papersave TM	1.1		0.83
6	1998	1913	Libertec TM	0.3		
7	1998	1968	Papersave TM	1.2	-0.2	1.65
8	2000	1893	Papersave TM	0.4		0.94
9	2000	1976	Papersave TM	0.6		0.75
10	2001	1931	Papersave TM	0.9		1.40
11	2002	1956	Papersave TM	1.0		0.91
12	2002	1976	Papersave TM	1.5		1.41
13 ^{**}	2004	1979	CSC Book Saver TM	10.4	10.5	
14	2005	1921	CSC Book Saver TM	0.2		
15	2005	1935	CSC Book Saver TM	0.4	-0.3	
16	2005	1964	CSC Book Saver TM	0.5		
17	2005	1979	CSC Book Saver TM	0.2		
18	2006	1896	CSC Book Saver TM	0.1		
19	2006	1934	CSC Book Saver TM	0.2		
20	2006	1939	CSC Book Saver TM	-0.2		
21	2006	1951	CSC Book Saver TM	-0.1	-0.7	
22	2006	1973	CSC Book Saver TM	0.2		

^{*} Value before subtracting the average acid content of non-deacidified papers, i.e. uptake of MgCO_3 (XRF).

^{**} Alkaline reserve was calculated as MgCO_3 although it could be CaCO_3 .

Operating conditions of GPC were the following; 1.00 ml/min of flow rate, 100 μl of injection volume, 45 minutes run time, DMAc/LiCl (0.9 %, w/v) after filtering through a 0.02 μm filter was used as eluant.

2.4.2 Accelerated ageing

A dynamic accelerated ageing method in a closed system was applied in this study. Conditions of accelerated ageing were the following: cycling of temperature between 45°C and 80°C every 6 hours without humidity control due to the technical limitation of the ageing chamber during the first 8 weeks followed by cycling tem-

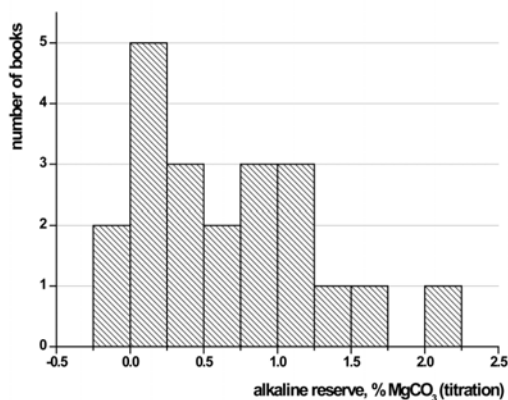


Fig. 2: Alkaline reserve (% w/w MgCO₃) determined by the standard titration method

perature between 20°C and 80°C every 6 hours with 50 % of relative humidity for the next 7 weeks.

3. Results and discussion

3.1 Alkaline reserve determined by titration

Table 1 shows the results obtained by titration and XRF for some samples. Alkaline reserve (% MgCO₃) of 21 books (No. 13 is excluded) measured with the standard titration method ranged from -0.2 % to 2.0 %. 52 % of the books met the requirements for alkaline reserve according to current DIN recommendation (0.5–2.0 % of MgCO₃) and 67 % of the books met the Swiss quality standard (0.3–2.3 % of MgCO₃ for original paper) (Fig. 2). Comparing our data to the Swiss National Library data, of which more than 95 % of tested items should meet the standard, many of the sample books have not been treated sufficiently. Books treated by the CSC Book Saver™ generally contained lower concentration of an alkaline deposit than those treated by the Papersave™. Only one of nine CSC Book Saver™ treated books met the current DIN recommendation.

Samples of No. 20 and No. 21 even show a negative alkaline reserve, i.e. they are still acidic. In case of No. 21, the non-deacidified duplicate book contained -0.7 % – meaning very acidic, and mass deacidification could only increase the value to -0.1 % which is not enough even for neutralising the existing acids. Another example is No. 15, containing 0.4 % of alkaline reserve after deacidification, its

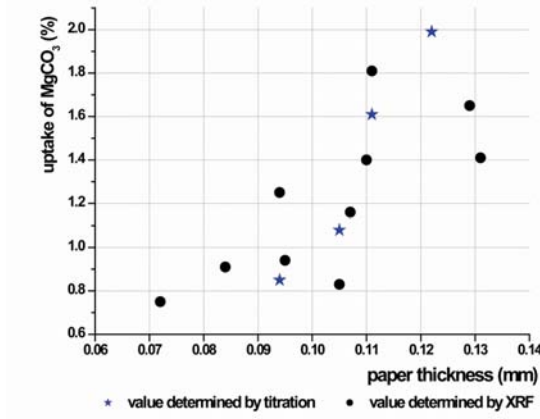


Fig. 3: Paper thickness vs. uptake of alkaline reserve (%) (only the Papersave™ treated books, value determined by titration (%) = $[\text{MgCO}_3]_{\text{deacidified book}} + |[\text{MgCO}_3]_{\text{non-deacidified duplicate}}|$, thickness was determined as an average value of five measurements.)

duplicate containing -0.3 %. It can be stated that the difference of 0.7 % was the amount of alkaline reserve introduced to the paper during the deacidification process, and as 0.3 % was consumed by neutralisation of acids, 0.4 % remained as an alkaline reserve.

The following simple equations explain how much magnesium carbonate can be measured as an alkaline reserve by titration after deacidification.

$$[\text{MgCO}_3]_{\text{AR}} = [\text{MgCO}_3]_{\text{uptake}} - [\text{MgCO}_3]_{\text{used for neutralisation}}$$

$$[\text{MgCO}_3]_{\text{used for neutralisation}} = [\text{Acids}]_{\text{exist}}$$

Consequently, there are two variables for real book papers: $[\text{MgCO}_3]_{\text{uptake}}$ and $[\text{Acids}]_{\text{exist}}$. $[\text{MgCO}_3]_{\text{uptake}}$ should be assessed by each deacidification company, determining the relation between concentration of alkaline compounds in the solution and uptake of alkaline reserve of various test papers which have known $[\text{Acids}]_{\text{exist}}$. $[\text{Acids}]_{\text{exist}}$ varies for real book papers. 11 non-deacidified books resulted in the average value of -0.3 % in our lab with variations from 0 % to -0.7 %. Paper from a large European city with polluted air quality can contain up to minus 0.82 % of magnesium carbonate (Blüher 2006), and Shahani and Harrison (2002) also observed 0.2 to 0.3 meq/g of acid concentration from their samples, which corresponds to about minus 1.25 % to minus 0.84 % of MgCO_3 . Therefore $[\text{Acids}]_{\text{exist}}$ has to be taken into account, especially when the process aims to deposit a relatively low amount of alkaline reserve. The previous examples, No. 15 and No. 21 showed that the uptake of magnesium car-

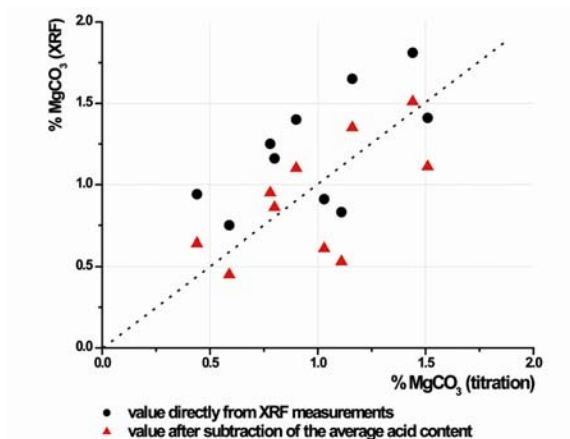


Fig. 4: Plot of % w/w MgCO₃ by titration vs. subtraction % w/w MgCO₃ by XRF

bonate was to similar each other as 0.7 % and 0.6 % respectively. However, one book met the Swiss quality standard while the other one did not.

In reality, mass deacidification service providers should consider not only the acidity of book papers before treatment, but also the uptake of alkaline reserve, since different types of papers absorb different amounts of alkaline reserve. Test papers can be designed to mimic acidity of original book papers, but the final alkaline reserve left can still be different from the original papers due to a large variation of the amount taken by the book. One of the factors differentiating the uptake of alkaline reserve can be paper thickness. Fig. 3 illustrates that the uptake of MgCO₃ somewhat correlates with paper thickness. Samples shown in this graph were treated by the Papersave™ process but not in the same batch. The difference in the uptake of alkaline reserve can be more than 1 %. Therefore paper properties such as thickness, density, permeability, etc. can lead to variations in the uptake of alkaline reserve. This is why original book samples with different physical properties should be included in to the paper sets used for quality control.

3.2 Alkaline reserve determined by XRF

Before discussing the amount of alkaline reserve determined by XRF (see 1.2), it should be noted again that alkaline reserve of the Papersave™ treated books determined using XRF is the amount of uptake and calculated on three assumptions; the acid content of original book papers are similar to test papers, no titanium exists in

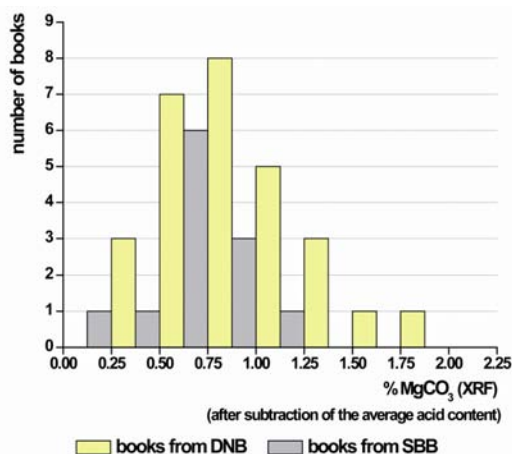


Fig. 5: Histogram of % MgCO₃ determined by XRF after subtracting the average acid content.

the sample prior to deacidification, and the uptake ratio of Ti and Mg is same to test samples (Ramin 2010). When comparing % of MgCO₃ determined by XRF to % of MgCO₃ determined by titration, a similar trend could be observed (Fig. 4). However, % of MgCO₃ determined by XRF is significantly higher compared to the value obtained by titration in most cases, and it tends to be still higher than the values determined by titration even after subtracting the average acid content, i.e. -0.3 % of MgCO₃, of original books before deacidification. In some cases, a significantly lower amount of MgCO₃ than the value determined by the titration was detected by XRF as well, which could be explained by a change in uptake ratio of Ti and Mg or less corresponding to the % MgCO₃ calibration versus Mg constituent. Therefore, it should be kept in mind that alkaline reserve determined by XRF as presented in the following Fig. 4 might overstate the actual amount of alkaline reserve in general.

When subtracted the average acid content measured in our lab to the data that is -0.3 % of MgCO₃ according to 11 non-deacidified books, 95 % of 40 books met the Swiss quality standard (0.3–2.3 % of MgCO₃ for original paper) and 88 % of the books met the DIN recommendation (0.5–2.0 % of MgCO₃). These books were all treated with the PapersaveTM process and therefore the amount of alkaline reserve is comparable to the results from the Swiss National Library (Reist 2006, Blüher 2006).

Factors other than the process causing variations in the amount of alkaline reserve were investigated. Fig. 6 left plots % MgCO₃ (XRF) against year of deacidification

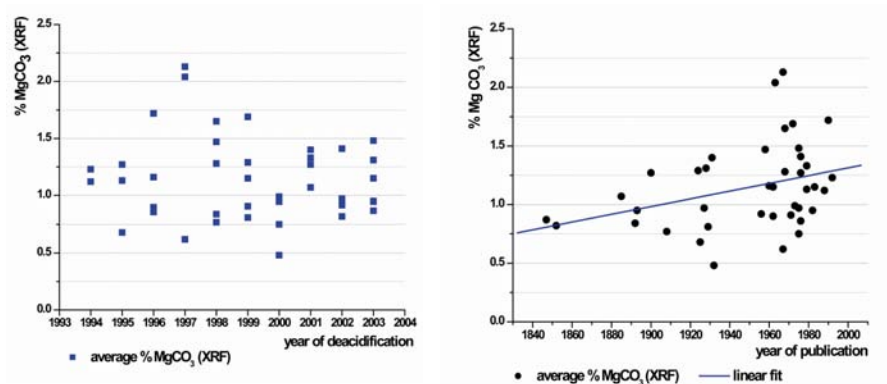


Fig. 6: % MgCO₃ (XRF) vs. year of deacidification and year of publication.

from 1994 to 2003 and indicates no distinctive trend that is corresponding to the trend of surface pH presented in part 1 (Ahn et al. 2011). On the other hand, again, the trend found in the amount of alkaline reserve with regard to year of publication corresponds to the result from surface pH measurements. That is more recently published books contain higher amounts of MgCO₃ (XRF) (Fig. 6). Books from SBB tend to contain lower amounts of alkaline reserve than books from DNB because books from SBB are generally older than books from DNB (Fig. 1), hence being more acidic and leaving less alkaline reserve.

3.3 Homogeneity of alkaline reserve determined by XRF

As XRF can measure MgCO₃ (XRF) on several spots of one single page, variations of uptake of alkaline reserve in a single page of a book could be easily measured. Figs. 7 and 8 illustrate four examples showing MgCO₃ (XRF, uptake) in different spots. Blue and red indicate amounts of ca. 0.3 % and 1.5 % respectively. Two examples in Fig. 7 show a homogeneous distribution of alkaline reserve within the page, regardless of how much MgCO₃ was taken up. In contrast to this, two examples in Fig. 8 show cases of a more heterogeneous distribution of alkaline reserve. In the case of 'Drewes' in Fig. 8 right, the quantity of MgCO₃ fluctuates from 0 % to 1.5 % with a standard deviation of 0.6, even though the book contains only about 100 pages in total.

Overall, 70 % of the books achieved standard deviations lower than 0.2, and 93 % of the books evaluated in this study can be regarded as successfully treated in terms

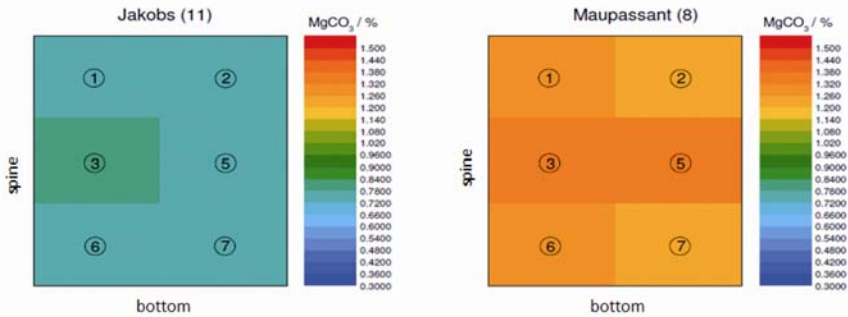


Fig. 7: Examples of homogeneous MgCO_3 (XRF) distribution within a single page. 'Jakobs' was published in 1975 and deacidified in 2000, and 'Maupassant' was published in 1968 and deacidified in 1998. Both are from the German National Library in Leipzig.

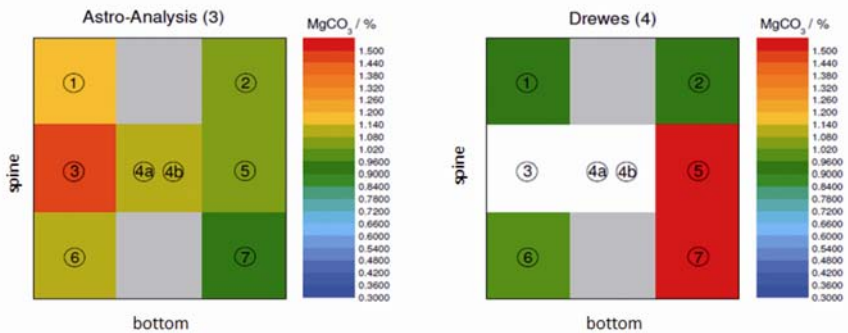


Fig. 8: Examples of inhomogeneous MgCO_3 (XRF) distribution within a single page. 'Astro-Analysis' was published in 1979 and deacidified in 1995, and 'Drewes' was published in 1976 and deacidified in 1996. Both are from the German National Library in Leipzig.

of homogeneity, according to the Swiss quality standard that requires a standard deviation lower than 0.5 (Fig. 9). The Swiss quality standard is not too strict here – when standard deviation is higher than 0.2, more than 0.5 % of MgCO_3 between spots is still acceptable. For example, in the case of 'Astro-Analysis' in Fig. 8 left, which showed variations from 0.91 % to 1.47 %, the standard deviation of 6 measurements was 0.18.

Having no reliable scientific information on the long term effects of inhomogeneity of alkaline reserve on paper as well as no quality standards except the Swiss quality standard, it is hard to judge to what extent inhomogeneity can be considered acceptable. Inhomogeneous treatments of one single page after mass deacidification

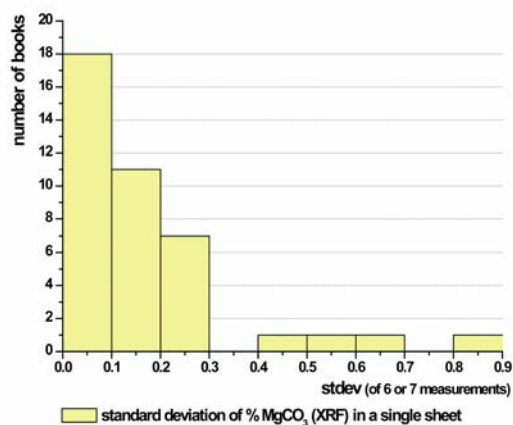


Fig. 9: Histogram showing homogeneity of alkaline reserve within a single page according to standard deviation of % MgCO_3 determined by XRF

have been detected by analysing alkaline reserve (Mg constituent to be more precise) and reported in many publications (Banik 2004, Daniel et al. 1994, Wagner 2008). This phenomenon seems to be more related to the deacidification process parameters such as pre-conditioning step or drying step after treatment (Kelly and Fowler 1978, Banik 2004), which means that it can be a characteristic for each process. As the treatment is carried out on a ‘mass’ scale, achieving equal conditions in every part of the book at the same time can be limited. Nonetheless, a homogeneous treatment should be aimed with clearly defined quality standards.

3.4 Alkaline reserve distribution assessed by SEM-EDX

Presence and distribution of the alkaline reserve within a local area of the surface of deacidified papers were examined together with their non-deacidified duplicates for comparison by SEM-EDX. Figs. 10–12 show SEM images of an approximately 1*1 mm area of the paper surface treated by three different deacidification processes. The LibertecTM treated paper contained particles that varied in size from several microns to several ten microns all over the surface. The LibertecTM process is supposed to deposit magnesium oxide onto the paper surface which forms hydroxides or carbonates during the wet reconditioning step and eventually permeates into the paper (Libertec 2011). The reaction is, in theory, promising. However, the mechanisms from formation of hydroxide or carbonate to neutralisation of acids existing

in the paper are not sufficiently verified. The process seems to be more feasible when a certain level of humidity higher than 50-55 % of relative humidity recommended for museum or archives by Thomson (1994) and Grattan and Michalski (2011) is present (Polovka et al. 2006). The irregular sizes and shapes of magnesium oxide on the LibertecTM treated paper could make the process even less promising because the adsorption of water onto the surface of magnesium oxide relates to the particle size and morphology (Zumbuehl and Wuelfert 2001, Polovka et al. 2006). Besides, an inhomogeneous whitish deposit (presumably magnesium oxide) could be observed on the treated paper even with the naked eye and can be removed easily. This will lead to high pH levels, especially on the surface, as confirmed in our surface pH measurements (Ahn et al. 2011). Consequently, the effect of the LibertecTM process should be re-examined. In contrast, the CSC Book SaverTM treated paper and the PapersaveTM treated paper hardly showed any deposits, suggesting magnesium alkali substances formed by these non-aqueous immersion systems penetrated into the fibre networks or are smaller than the detectable size as proposed smaller than 1 μm in the Battelle's early test (Wittekind, 1994). Comparing these surfaces to the non-deacidified duplicates, the overall appearance was similar. However, sizing material on the surface of the paper seems to have been leached out slightly after treatment (Figs. 11 and 12). The CSC Book SaverTM treated paper looked slightly more altered than the PapersaveTM treated sample. When applying a drop of water, the resulting water penetration areas were larger in deacidified books than in their non-deacidified duplicates, indicating that a loss of sizing can cause changes in the properties of paper such as permeability. The potential change or loss of original paper composites after a deacidification treatment in aqueous and non-aqueous immersion systems and its influence on paper properties should be investigated more comprehensively with extensive samples in the future.

Due to the undetectable particle size of the alkaline reserve of CSC Book SaverTM and PapersaveTM treated papers, distribution of magnesium substances was visualized using Mg element mapping.

All three papers seemed to generally feature a homogeneous Mg distribution on a local area (1*1 mm approx.). However, relatively more aggregated or larger Mg compounds could be observed on the LibertecTM treated paper, while the CSC Book SaverTM treated paper and the PapersaveTM treated paper exhibited much finer Mg compounds distributed evenly on the entire examined area. The amount of Mg on the CSC Book SaverTM treated paper appeared to be larger than on the PapersaveTM treated paper although % alkaline reserve determined by titration was 0.5 % of MgCO_3 lower. Figs. 14–16 illustrate the Mg distribution within the paper structure. Mg compounds could permeate into the paper matrix of the CSC Book SaverTM

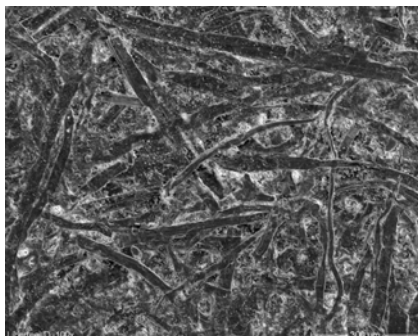
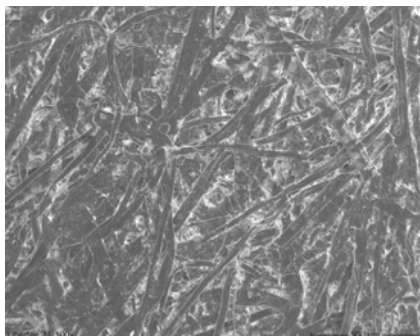


Fig. 10: SEM images of paper surfaces: non-deacidified (left) and deacidified by LibertecTM process in 1998 (right). Irregular size of alkaline reserve particles can be seen on the surface of the deacidified book.

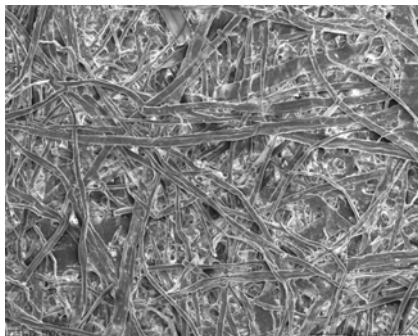
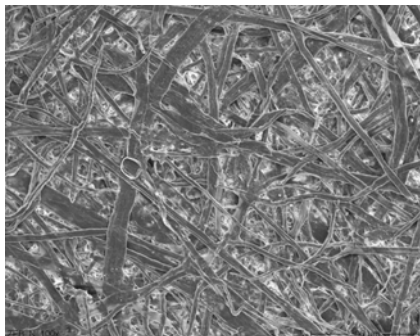


Fig. 11: SEM images of paper surfaces: non-deacidified (left) and deacidified by PapersaveTM process in 1998 (right). Alkaline reserve cannot be observed. Fibers are slightly more pronounced on the surface of the deacidified book than the non-deacidified book indicating loss of sizing.

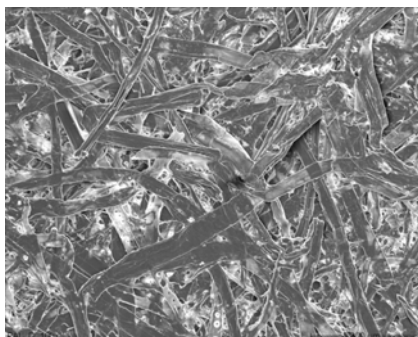
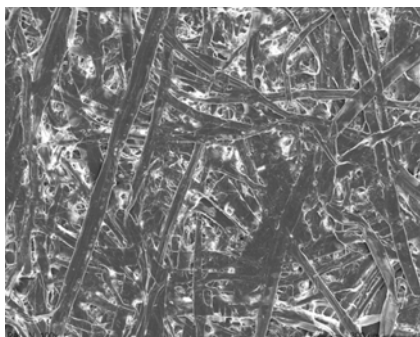


Fig. 12: SEM images of paper surfaces: non-deacidified (left) and deacidified by CSC Book SaverTM process in 2005 (right). Alkaline reserve cannot be observed. Fibers are slightly more pronounced on the surface of the deacidified book than the non-deacidified book like the case of the PapersaveTM process in Fig. 11.

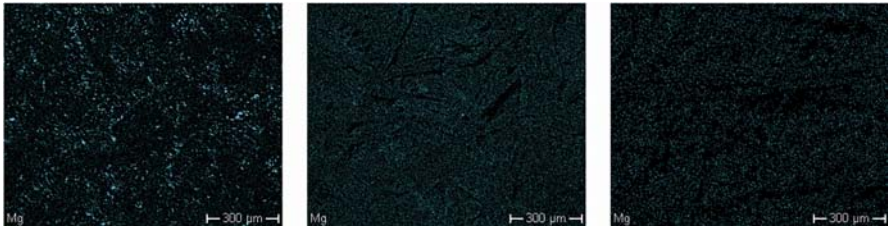


Fig. 13: Mg mapping of the same samples analysed by SEM-EDX. Sky blue areas indicate Mg. The Libertec™ treated book (left), The CSC Book Saver™ treated book (middle), and the Papersave™ treated book (right). All of them show homogeneous distribution of Mg. However, the Libertec™ treated one has irregular and relatively coarse size or aggregation of Mg whereas the CSC Book Saver™ and the Papersave™ show fine distribution of Mg on the surface.

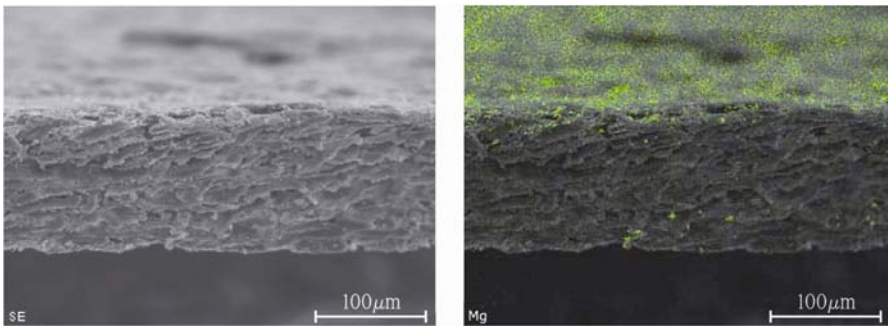


Fig. 14: Mg mapping of the cross-section of the Libertec™ treated paper. Green areas indicate Mg. Not much Mg is detectable on the cross-sectioned area of paper.

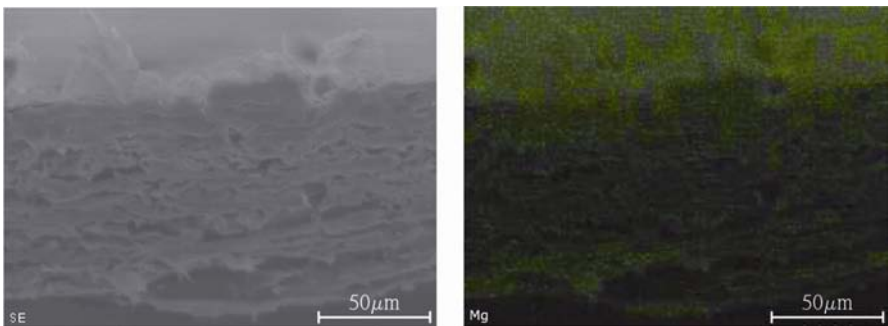


Fig. 15: Mg mapping of the cross-section of the CSC Book Saver™ treated paper. Green areas indicate Mg. Mg is distributed into the paper matrix. However, the constituent of Mg in the core area of the cross-sectioned paper is less than the area close to the surface.

treated paper, but did not penetrate to its very core (Fig. 15), which may explain why the amount of Mg was relatively high on the surface (Fig. 13 middle). The Paper

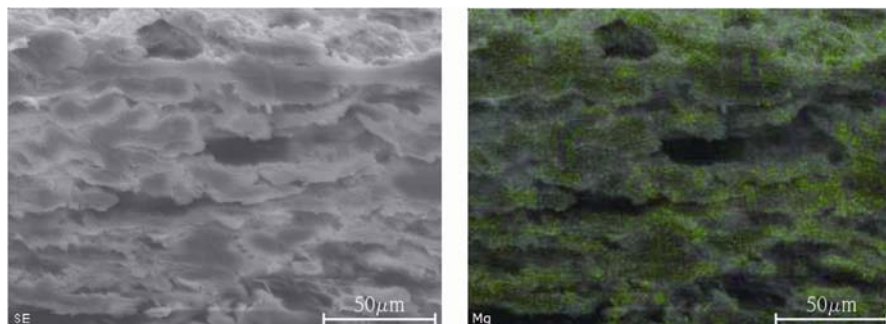


Fig. 16: Mg mapping of the cross-section of the Papersave™ treated paper. Green areas indicate Mg. Homogenous distribution of Mg throughout the paper matrix can be seen.

save™ treated paper showed an even Mg distribution throughout the cross-sectioned area which is one of benefits of the immersion system. In contrast, the Libertec™ sample showed little penetration or dispersion of Mg compounds into the paper structure. Homogenous Mg distribution into the paper structure was reported for both CSC Book Saver™ and the Papersave Swiss™, and it was found to be an important parameter when trying to improve the benefits from deacidification treatment (Ramin et al. 2009). Although our results are based on the examination of only one paper for each respective process, they still reflect the efficiency of the three processes in terms of distribution of alkaline reserve over the surface and its penetration into the paper matrix or fibre networks.

3.5 Optimum amount of alkaline reserve for cellulose stability

Although several quality standards suggest a range of alkaline reserve to be deposited after deacidification, there are almost no systematic studies on the specific amount of alkaline reserve capable of enhancing long-term stability of cellulose. In this study defining the optimum amount of alkaline reserve was attempted, based on real library books treated with different deacidification processes. The distribution and integrity of cellulose chains, as measured using GPC which can be considered the most intrinsic parameter for paper stability served as the decisive factor.

For the first time, the interplay of the amount of alkaline reserve deposited and cellulose stability was investigated using library materials.

Regardless of the very different conditions of the books such as different deacidification parameters, differences in paper making, age, damage, etc., a correlation between the amount of alkaline reserve and cellulose stability was found as shown in Fig. 17. Higher amounts of alkaline reserve of up to around 1.5 % of MgCO_3 decreased the

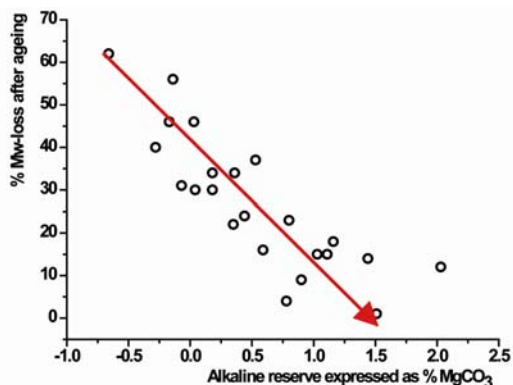


Fig. 17: Alkaline reserve (% w/w MgCO₃ by titration) vs. Mw loss (%) after accelerated ageing

loss in weighted average molecular weight (Mw) of cellulose after accelerated ageing considerably. The Mw-loss after ageing was calculated after confirming that there was no significant difference in Mw between the deacidified paper and the non-deacidified duplicate book before ageing (i.e. whether the same paper was used in both books could be confirmed by similar molecular weight distributions).

It can therefore be concluded that a higher alkaline reserve results in significantly more stable cellulose in the long run. The beneficial effect of higher alkaline reserve by far outbalanced any accompanying negative effects. Concerns that additional damage may be caused when depositing higher amounts of alkaline reserve, which led to a more moderate introduction of base in European mass deacidification processes could not be verified in this study. On the contrary, increasing the amount of alkaline reserve to values around 1–1.3 % MgCO₃- contrary to the lower limits of the standards, i.e. 0.3 % for the Swiss quality standard and 0.5 % for the current DIN recommendation would greatly enhance cellulose stability – always keeping in mind that there are other factors influencing the concentration of deacidification agents. This alkaline reserve must be evenly distributed over the whole volume of the paper sheet and not merely accumulate on its surface. In fact, the LibertecTM process hardly contributed to the reduction of Mw-loss during accelerated ageing, although a certain amount of alkaline reserve was present.

4. Conclusions

The alkaline reserve of 52 deacidified books from the German National Library in Leipzig and the Berlin State Library was assessed for the first time using various methods. 67 % of 21 books measured by the titration method met the Swiss quality

control standard (0.3–2.3 % of MgCO_3 for original papers) and only 52 % met the current DIN recommendation (0.5–2.0 % of MgCO_3). Most of the books not meeting the standards contained lower amounts of alkaline reserves and had been treated by the CSC Book SaverTM process, which indicates that the process constitutes the main factor influencing alkaline reserve. Considering the Swiss quality standard requires that 95 % of the tested books should be within the defined range, the amount of alkaline reserve in the treated books of both libraries was not sufficient. XRF analysis of MgCO_3 in 40 books revealed that after deduction of the average acid content, 95 % of the books met the Swiss quality standard and 88 % of the books met the DIN recommendation. According to XRF analysis, books from the Berlin State Library contain relatively lower amounts of alkaline reserve than books from the German National Library in Leipzig, which can be explained by their earlier year of publication. 93 % of 40 books can be considered homogeneously treated according to the Swiss quality standard concerning the distribution of the alkaline reserve throughout one single page. Since the homogeneity of alkaline reserve is directly related to process parameters, quality standards for homogeneity have to be established or adjusted for each process through further testing.

The objective should be a higher amount of alkali reserve than the lower limit the standard defines in order to take into account natural variations of the acid content before deacidification as well as the capacity of alkali uptake of papers. This is even more important since we could clearly demonstrate that the optimum amount of alkaline reserve for long-term prevention of cellulose depolymerisation ranges between 1 % and 1.3 % MgCO_3 .

Moreover, it is crucial to have the alkaline reserve evenly distributed throughout the whole volume of the paper rather than just over its surface. SEM-EDX analysis on a local area of papers treated by LibartecTM, PapersaveTM, and CSC Book SaverTM supported the data obtained for cellulose stability after accelerated ageing. CSC Book SaverTM and PapersaveTM yielded satisfactory cellulose stability in most cases, which corresponded to the homogeneous distribution of Mg over the surface and also within the paper matrix. Within the non-aqueous immersion processes, PapersaveTM achieved better results regarding alkaline reserve and cellulose integrity, which was also reflected in the distribution of Mg-ions. On the other hand, LibartecTM treated paper exhibited Mg substances in uneven sizes and shapes on the surface and almost no trace of impregnation of Mg substances into the paper structure.

For the future of mass deacidification methods, the determination of alkaline reserve will have to be improved in order to manage large quantities of samples in quality control on one hand, and to assess alkaline reserve throughout the paper matrix, as well as at the surface, on the other. From the viewpoint of cultural heritage

this method should involve only non-invasive or micro-invasive sampling techniques. Based on the results presented in this study, an overall higher amount of alkaline reserve should be taken into consideration for future limits in standards and protocols.

Acknowledgement

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Zusammenfassung

Nachhaltigkeit der Massenentsäuerung – Teil II: Alkalische Reserve

Die alkalische Reserve kann als der entscheidende Parameter für die Beurteilung der Massenentsäuerung angesehen werden, nachdem die Menge, die durch einen entsprechenden Prozess im Papier deponiert wird, für die Nachhaltigkeit der Behandlung von maßgeblicher Bedeutung ist. In diesem Beitrag werden Resultate präsentiert, die bei der analytischen Bestimmung der alkalischen Reserve an Büchern gemessen wurden, die in der Zeit von 1994 bis 2006 einem Massenentsäuerungsverfahren unterzogen worden sind. Die Bücher entstammen den Sammlungen der Deutschen Nationalbibliothek (DNB) und der Staatsbibliothek zu Berlin – Preußischer Kulturbesitz (SBB). Bedauerlicherweise ist die Bestimmung der alkalischen Reserve in Papier nur mit aufwändigen und zeitintensiven Verfahren möglich. Es wurden daher die verschiedenen Techniken miteinander verglichen, darunter die Bestimmung mittels Titration entsprechend ISO 10716:1994, XRF zur Ermittlung der Verteilung von Magnesium und SEM-EDX für die Untersuchung der Verteilung der alkalischen Reserve in der Papiermatrix. Unter den angeführten Methoden wird zur Zeit nur die arbeitsaufwändige Titration als Verfahren für die Beurteilung des Behandlungserfolgs allgemein akzeptiert. Darüber hinaus wurde der Einfluss der gemessenen Menge der alkalischen Reserve in behandelten Büchern auf die Stabilität der Cellulose nach künstlicher Alterung mittels Molekulargewichtsbestimmung evaluiert.

Es konnte festgestellt werden, dass durch Massenentsäuerung nur in 52% der untersuchten Bücher eine alkalische Reserve eingebracht werden konnte, die in ihrer Größenordnung das in den DIN Empfehlungen angeführte untere Limit von 0,5% Magnesiumcarbonat erreichte. Als limitierende Faktoren für die Einbringung einer ausreichenden Menge der alkalischen Reserve mittels Massenentsäuerung wurden einerseits die angewandten Verfahren und andererseits das Alter der behandelten Bücher identifiziert. Der CSC Booksaver-ProzessTM und der Papersave-Prozess® ermöglichten das Einbringen von alkalischen Magnesiumverbindungen in gleichmäßiger und fein verteilter Form in die Papiermatrix, im Gegensatz dazu erschien die mittels Libertec® eingebrachte alkalische Reserve ungleichmäßig und grobkörnig auf der Oberfläche der Papiere verteilt. Das effektivste Verfahren in Bezug auf die Einbringung einer alkalischen Reserve in die Papiermatrix war gemäß den Untersuchungen der Papersave Prozess®. Die Korrelation der eingebrachten alkalischen Reserve mit der Bestimmung der Molekulargewichtsverteilung der Cellulose vor und nach der künstlichen Alterung ließ eine direkte Beziehung zwischen der Menge der alkalischen Reserve und dem durch Alterung eintretenden Celluloseabbau erkennen. Auf der Basis der erhaltenen Resultate wird vorgeschlagen, eine größere Menge an alkalischer Reserve (0,8-1% Magnesiumcarbonat) als Min-

destanforderung für eine erfolgreiche Behandlung mittels Massenentsäuerung in den Qualitätsstandards zu definieren.

Résumé

Authors and contacts

Kyujin Ahn gained a MSc. in conservation science at De Monfort University in Leicester, U.K. in 2000. From 2001 to 2003 she took a Mellon fellowship at Los Angeles County Museum of Art after an internship at Victoria and Albert Museum, and was employed at Samsung Museum of Art, Leeum in Seoul, Korea until 2008. She is currently doing a PhD under Prof. Potthast at the University of Natural Resources and Life Sciences, Vienna (BOKU Wien).

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Paper III

**Is cellulose degradation
due to β -elimination
processes a threat in mass
deacidification of library
books?**

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Is cellulose degradation due to β -elimination processes a threat in mass deacidification of library books?

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Abstract As papers become acidic and brittle over time, libraries apply mass deacidification processes to their collections in order to neutralize acids and deposit an alkaline reserve in the paper. Books commonly treated by mass deacidification have undergone natural aging of up to 150 years. The risk of alkali-induced degradation of cellulosic material upon mass deacidification remains uncertain. In the present study, the extent of β -elimination-type degradation reactions was investigated by comparing deacidified and non-deacidified counterparts, using deacidified library materials and identical issues of non-deacidified books from second-hand book shops. The study dealt with only naturally-aged papers focusing on investigation of immediate effects of mass deacidification rather than a long-term impact. Gel permeation chromatography coupled with carbonyl group labeling gave insight into cellulose chain cleavage as well as into the behavior of oxidized functionalities. Processes occurring under natural aging conditions were compared to those upon

artificial oxidation of model pulps. Library books did not show a significant reduction in molecular weight after mass deacidification compared to the non-deacidified controls, which stands in contrast to oxidized model pulps. The models showed a more pronounced loss of molecular weight upon deacidification treatments. A decrease in carbonyl groups other than reducing ends was found to occur. Thus, oxidized functionalities were found to be reactive in mass-deacidification reactions; the different behavior was traced down to particular regions of oxidative damage along the cellulose chains. In general, β -elimination processes did not pose a large risk factor upon mass deacidification treatments of the naturally-aged library material tested.

Keywords β -Elimination · Oxidation · Carbonyl groups · Molecular weight Cellulose degradation · Historic books Paper · Mass deacidification

Introduction

Processing methods and sizing agents used in paper-making, especially between 1850 and 1980, caused the formation of acidic compounds that deteriorate the paper over time. In the 1990s, mass deacidification operations were commenced to tackle this problem. Mass deacidification is performed at the ton scale, as compared to the small-scale, more tedious classical conservation treatments. Its purpose is to neutralize existing acids in

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documents and papers and simultaneously introduce an alkaline reserve to prevent the resumption of acidic degradation. Since the application of magnesium methoxide in a mixture of methanol and different freons was developed as a non-aqueous deacidification method in the US in the 1970s (Kelly et al. 1977), many countries in Europe and North America have started to develop mass deacidification processes. Those that were found to be technically feasible on a larger scale went commercial, and have been applied to the collections of libraries and archives since the 1990s (Porck 1996; Banik 2005; Porck 2006; Grossenbacher 2006; Gerlach 2006; Blüher 2006; Stumpf 2006; Andres et al. 2008; LOC 2011). As an example, the Swiss National Library treats about 40 tons of books and archive documents annually (Grossenbacher 2006), the Central and Regional Library Berlin has treated 45,000 books as of 2005 (Gerlach 2006).

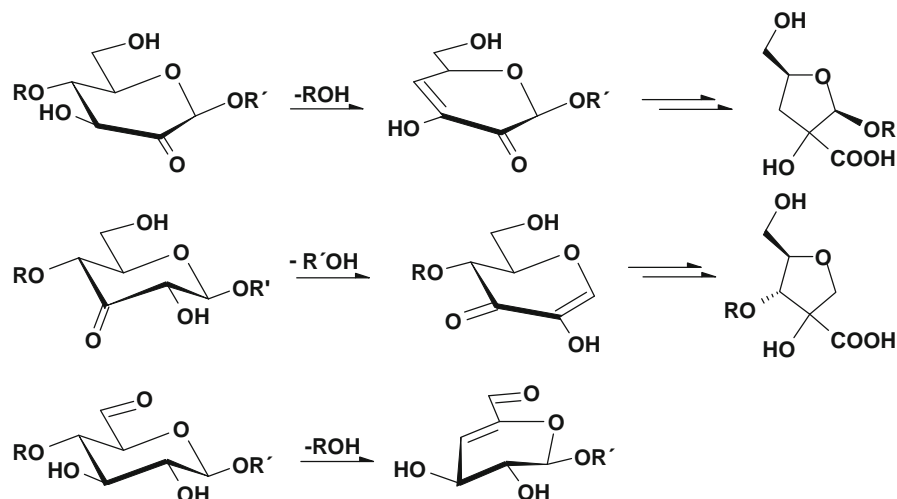
Mass deacidification processes can be classified according to the carrier medium, the deacidification agent, and the type of treatment: aqueous liquid immersion (BückerburgTM), non-aqueous liquid immersion (PapersaveTM, CSC-BookSaverTM), non-aqueous liquid suspension (BookkeeperTM), and dry application of sub-micron particles (LibertecTM). More details on mass deacidification processes have been summarized in the literature (Porck 1996; Blüher and Vogelsanger 2001; Banik 2004; Libertec 2007).

Mass deacidification generally consists of four steps: drying (pre-conditioning), deacidification (treatment), post-drying, and reconditioning. Drying (pre-conditioning) involves reduction of the moisture content of paper under vacuum to enhance the uptake

of reagent and lower the extent of moisture-driven side reactions. The actual deacidification is an impregnation step transporting the active agent into the paper. The neutralization of acids present in paper commences in this step. The post-drying step is necessary to remove residual solvent and other volatiles, often under vacuum. Finally, the reconditioning step is important to complete formation of alkaline reserves and recovery of the ambient moisture content of the paper.

The alkaline treatment of aged paper materials (books and archive documents) has raised the question of whether a high pH poses the threat of alkaline degradation due to β -elimination in the cellulose. The β -elimination reaction in general starts from an oxidized functionality, such as a keto or aldehyde group. Nucleophilic attack by a hydroxyl ion at this position causes the substituent in the β -position to be eliminated (Fengel and Wegener 1984). If the oxidation takes place at the cellulose level, the elimination reaction might result in cleavage of the glycosidic bond, and thus chain scission. Model studies on oxidized model pulp or paper have demonstrated the possibility that cellulose degradation may occur during a deacidification treatment (Kolar and Novak 1996; Bogaard and Whitmore 2001; Malesic et al. 2002; Stephens et al. 2009). Generally, higher carbonyl group content was found to yield a larger risk. The uncertainty as to whether or not β -elimination occurs during mass deacidification has already resulted in recommendations of lower quantities of alkaline reserve to be deposited, that is 0.06–0.24 mol/

Fig. 1 Cleavage of the glycosidic bond by β -elimination starting at the oxidized structures along the cellulose (according to Lewin 1997)



kg (0.5–2 % of MgCO_3) (Hofmann and Wiesner 2011), in order to avoid possible harm to the books.

Figure 1 depicts the most likely carbonyl motifs in anhydroglucose units (AGU) of cellulose (C2–C3-dialdehyde structures as formed upon periodate oxidation of cellulose are not considered to be generated during natural aging) and their reaction products upon β -elimination. In the case of a C-6 aldehyde being present, the cellulose chain is split at the C-4, yielding a novel reducing end group at the eliminated chain end and a rather stable fragment with a conjugated double bond. A structure with a C-2 keto group will also eliminate the chain substituent at C-4, again producing a novel reducing end in addition to an unstable enol-enone fragment, which undergoes rearrangement into the corresponding acid. Oxidation at C-3 of the AGU results in elimination of the chain at C-1. In this case, no new reducing end is produced, and the original keto group is rearranged into a non-reducing acid. The keto group at C-2 and C-3 cannot be considered to be fixed, as these sites tend to interchange in alkaline pH due to keto-enol tautomerism.

Based on these reactions, the C-6 aldehyde and the C-2 keto are active carbonyls that, upon β -elimination and chain cleavage under alkaline conditions, generate new reducing ends and thus can cause further degradation, whereas the C-3 keto is considered a non-active carbonyl that induces chain scission, but no formation of new reducing ends and no further degradative reactions (Lewin 1997; Potthast et al. 2006). All of this, however, mainly applies to the end-wise peeling reaction at elevated temperatures (Fengel and Wegener 1984; Knill and Kennedy 2003; Potthast et al. 2006). The end-wise peeling reaction and its subsequent reactions can be considered very slow during mass deacidification, which operates at temperatures below 30–40 °C. Moreover, as it proceeds from the reducing end, it causes only rather negligible chain shortening. By contrast, the analogous reactions starting from carbonyl functions along the chain proceed readily at ambient temperatures (and are thus also relevant for mass deacidification conditions) and, furthermore, might cause severe fragmentation and chain shortening.

The risk of alkaline degradation induced by a deacidification treatment has been examined in several studies with model pulps or papers that were artificially oxidized, focusing mainly on aqueous

deacidification treatments (Kolar and Novak 1996; Bogaard and Whitmore 2001; Malesic et al. 2002; Stephens et al. 2009). Aside from the fact that the question of how well artificially-aged model papers reflect their naturally-aged book counterparts, no investigation on real books deacidified at a mass scale with commercial non-aqueous systems has been presented so far, although tons of books have been treated this way up to now.

In this paper, we would like to address the risk of cellulose degradation by β -elimination during mass deacidification by means of original library book samples that have been deacidified in the last two decades. These naturally-aged papers are compared on the one hand with model pulps that were deacidified in the same way and, on the other hand, with the same books that did not undergo a mass deacidification treatment.

Materials and methods

Model pulp and mass deacidification treatment

Bleached beech sulfite pulp was used as a model pulp. The pulp was oxidized by sodium hypochlorite (Fluka) buffered at pH 7 with a 0.2 M phosphate buffer. Hypochlorite (13 % active chlorine) was used at a dosage of 0.5 ml per gram of pulp. Temperature (30 °C) and pH were continuously checked for constancy during the reaction. The reaction time was 30 and 60 min. Pulp hand sheets were made at Lenzing AG (www.lenzing.at) according to ISO 3688:1999 (ISO 2003). Both non-oxidized and oxidized pulps were treated in five different batches of the CSC Book SaverTM mass deacidification process offered by PAL (Preservation Academy GmbH), Leipzig, Germany. The presented data after deacidification are the average values of five samples.

Sample preparation for GPC

CCOA (carbazole-9-carbonyl-oxy-amine) labeling of carbonyl groups, and FDAM (9H-fluoren-2-yl-diazomethane) labeling of carboxyl groups, was performed as described earlier (Röhring et al. 2002a; Röhring et al. 2002b; Potthast et al. 2003; Bohrn et al. 2006). For the library books, half the sample amount (25 mg

of wet sample) relative to that of the standard method was used. After labeling of the samples, dissolution in *N,N*-dimethylacetamide/lithium chloride 9 % (w/v) (DMAc/LiCl) was achieved via solvent exchange at room temperature. Measurements were performed with a GPC-MALLS detector system that yields both molecular weight and molecular weight distribution in addition to the amount of oxidized groups. Samples to be compared were prepared and measured in the same batch with a reference paper.

GPC conditions

The GPC system used consists of a fluorescence detector (TSP FL2000) for monitoring the CCOA label, a Shimatsu RF 535 for the FDAM label, a multiple-angle laser light scattering detector (MALLS) [Wyatt Dawn DSP with argon ion laser ($\lambda_0 = 488$ nm)], and a refractive index detector (Shodex RI-71). Four serial GPC columns (Polymer LaboratoriesTM (now VarianTM/AgilentTM) PLgel mixed-ALS, 20 μ m, 7.5 \times 300 mm) were used as the stationary phase. A degasser (Dionex DG-2410), autosampler (HP 1100), pulse damper pump (Kontron pump 420), and column oven (Gynkotech STH 585) were also parts of the system.

Operating conditions of the GPC: 1.00 ml/min flow rate, 100 μ l injection volume, 45 min run time, $\lambda_{\text{ex}} = 290$ nm and $\lambda_{\text{em}} = 340$ nm for fluorescence detection of the CCOA label, and $\lambda_{\text{ex}} = 280$ nm and $\lambda_{\text{em}} = 312$ nm for fluorescence detection of the FDAM label. DMAc/LiCl (0.9 %, w/v), filtered through a 0.02 μ m filter, were used as the eluant.

Data evaluation was performed with standard Chromeleon, Astra, and GRAMS/32 software packages. From the total amount of carbonyl groups obtained by GPC, REG (reducing end groups) and along-chain carbonyl contents were calculated. As REGs can be calculated from Mn (number average molecular weight) on the assumption that determination of Mn is correct and no REGs are converted to acids by previous oxidation (Potthast et al. 2008), a value of along-chain carbonyl content can be generated by the following equation: Along-chain carbonyl content ($\mu\text{mol/g}$) = total carbonyl content ($\mu\text{mol/g}$) – REG ($\mu\text{mol/g}$).

According to results from standard pulps ($N \sim 500$), the standard deviation for carbonyl group determination is below 5 %, for Mw about 5 %, and for Mn around 10 %.

Sample papers and mass deacidification treatment

Table 1 provides a list of the sample books in our study. In 2009, 25 deacidified books were selected from the German National Library in Leipzig and the Berlin State Library. Their duplicates were obtained from second-hand markets in Central Europe and analyzed together with the deacidified books. Three different mass deacidification processes were applied: one book was treated with a dry system, the LibertecTM process, and 24 books were treated with two different non-aqueous immersion systems, the CSC Book SaverTM process and the PapersaveTM process. The PapersaveTM process is based on liquid infiltration of a solution of titanium-magnesium ethoxylate in hexamethyldisiloxane, while the CSC Book SaverTM process uses a solution of carbonated magnesium propylate in *n*-propanol. The LibertecTM process takes advantage of mainly sub-micron-sized magnesium oxide dispersed in a dry air stream.

Results and discussion

β -elimination of model pulps upon mass-deacidification

Before analyzing real book papers, β -elimination of model pulps after mass deacidification was investigated. As a result of oxidation of the model pulps with sodium hypochlorite at pH 7, the carbonyl group content increased to 34.5 $\mu\text{mol/g}$ after 30 min of oxidation and to 45.9 $\mu\text{mol/g}$ after 60 min of oxidation, from an initial value of 18.1 $\mu\text{mol/g}$. The pulp before oxidation did not show any significant degradation after the mass deacidification treatment (Fig. 2, left). The oxidized pulps shifted their molecular weight distributions noticeably towards lower Mw regions due to β -elimination (Fig. 2, right). Figure 3 illustrates the relationship between Mw loss and the starting total carbonyl content of the oxidized and non-oxidized model pulps. Non-oxidized model pulps with an initial Mw of 314 kg/mol showed little change in Mw after the treatment, while 30-min oxidized pulps and 60-min oxidized pulps decreased their Mw from 219 to 193 kg/mol and from 185 to 156 kg/mol respectively. The higher the carbonyl group content, the more vulnerable the pulp to β -elimination due to deacidification. Therefore, β -elimination is dependent

Table 1 List weight of sample books

Sample No.	Year of publication	Year of deacidification	Deacidification process	Sample No.	Year of publication	Year of deacidification	Deacidification process
1N	1892			17N	1968		
1D	1892	1998	Papersave™	17D	1968	1998	Papersave™
2N	1893			18N	1958		
2D	1893	2000	Papersave™	18D	1958	1998	Papersave™
3N	1951			19N	1975		
3D	1951	2006	CSC Book Saver™	19D	1975	2000	Papersave™
4N	1913			20N	1976		
4D	1913	1998	Libertec™	20D	1976	2000	Papersave™
5N	1912			21N	1956		
5D	1912	1998	Papersave™	21D	1956	2002	Papersave™
6N	1935			22N	1976		
6D	1935	2005	CSC Book Saver™	22D	1976	2002	Papersave™
8N	1975			23N	1934		
8D	1975	2000	Papersave™	23D	1934	2006	CSC Book Saver™
10N	1992			24N	1979		
10D	1992	1994	Papersave™	24D	1979	2004	CSC Book Saver™
11N	1976			25N	1964		
11D	1976	1995	Papersave™	25D	1964	2005	CSC Book Saver™
13N	1962			26N	1979		
13D	1962	1996	Papersave™	26D	1979	2005	CSC Book Saver™
14N	1960			AN	1986		
14D	1960	1996	Papersave™	AD	1986	1994	Papersave™
15N	1963			BN	1912		
15D	1963	1997	Papersave™	BD	1912	2000	Papersave™
16N	1970						
16D	1970	1998	Papersave™				

N non-deacidified books, *D* deacidified books

on the content of carbonyl groups in the model pulps, and mass deacidification causes degradation of cellulose in the oxidized model pulp.

The content of total carbonyl groups was reduced after deacidification when the pulp was oxidized (Table 2), indicating consumption due to the high pH. Similar behavior was also found under more alkaline conditions (Potthast et al. 2006). However, higher reduction of the carbonyl group content after deacidification does not necessarily mean more degradation due to β -elimination, since both oxidized pulps (30 and 60 min) reduced the total carbonyl group content comparably. The content of uronic acids is not affected, as expected.

Book papers: Natural aging and β -elimination after mass deacidification

More than 10 years of mass deacidification did offer the chance to evaluate, with the sensitive methods available, whether a beneficial effect of mass deacidification can already be detected after that time, and whether β -elimination does really occur as a consequence of the treatment. For this purpose, books deacidified from 1994 to 1998 were studied first among the sample books. Thus, these books all underwent more than 10 years of natural aging after deacidification. They were compared to duplicate books obtained from the second-hand book market

Fig. 2 Molecular weight distribution (MWD) of model pulps before and after mass deacidification treatment. *Left* MWD of non-oxidized pulp. *Right* MWD of oxidized pulp

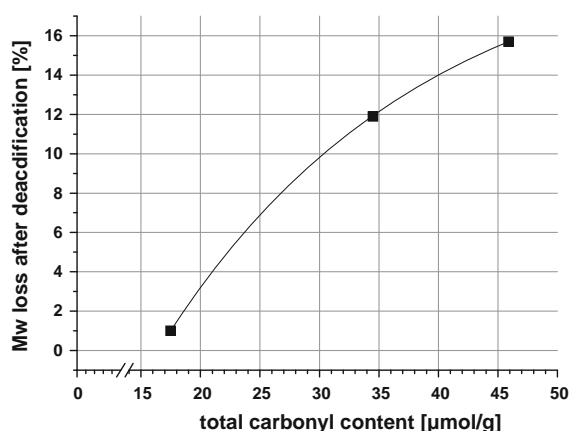
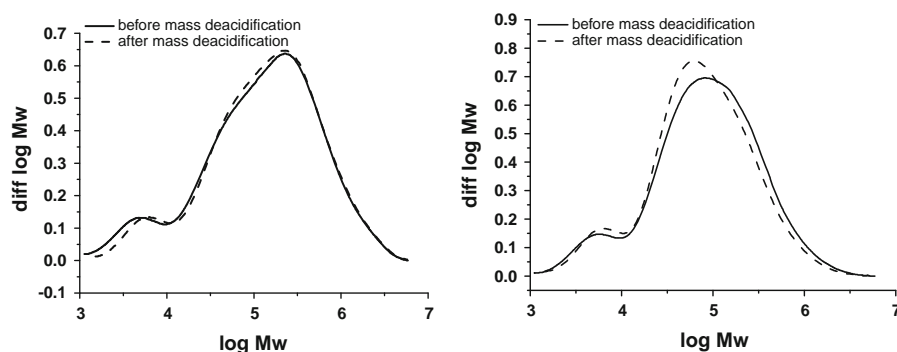


Fig. 3 Mw loss (%) of the oxidized model pulps right after mass deacidification versus total carbonyl content ($\mu\text{mol/g}$)

that were not deacidified. The publication dates of the books chosen ranged from 1892 to 1992. Figure 4 shows the weighted average molecular weight (Mw) determined by GPC measurements. Data analysis of all books analyzed showed no significant difference between deacidified and non-deacidified sets in Mw (average of 278 kg/mol vs. average of 281 kg/mol respectively). This parameter is currently the most sensitive indicator of cellulose degradation (lowest levels of RSD), especially when based on GPC-MALLS analysis. Thus, in real book samples, natural

aging of 10 years under library conditions neither showed cellulose degradation nor increased stability due to mass deacidification treatment.

The decrease in Mw after mass deacidification, as seen in the case of the oxidized model pulp (see Fig. 2, right), was not visible in the real book samples.

For example, set No. 14, published in 1960, changed the MWD only slightly after deacidification (Fig. 5, left), showing no sign of degradation. Only two books out of 25, regardless of the time of deacidification, showed significant degradation in the area of higher molecular weight (Fig. 5, right).

While the trend for molecular weight loss was different between the model pulps and the real book papers, a similar tendency was observed for the total carbonyl content, cf. Fig. 6, left. Comparing the samples, the along-chain keto/aldehyde groups, i.e., those not originating from the reducing ends, are lower for the deacidified samples (Fig. 6, right). This trend was also observed for more severe alkaline treatments of oxidized celluloses (Potthast et al. 2006). Since the oxidized model pulp has about the same total content of carbonyl groups compared to the book samples, the nature, i.e., the position of, the carbonyl must be different between oxidized model pulps and naturally-aged book samples. The position of the oxidation is crucial with regard to the AGU and the cellulose chain,

Table 2 Contents of the oxidative functionality groups of the bleached sulfite model pulp before and after mass deacidification

	Non-oxidized		Oxidized for 30 min		Oxidized for 60 min	
	Carbonyl ($\mu\text{mol/g}$)	Uronic A ($\mu\text{mol/g}$)	Carbonyl ($\mu\text{mol/g}$)	Uronic A ($\mu\text{mol/g}$)	Carbonyl ($\mu\text{mol/g}$)	Uronic A ($\mu\text{mol/g}$)
No treatment	17.5	18.0	34.5	19.7	45.9	22.7
After mass deacidification ^a	18.1	18.2	30.5	20.6	42.5	23.4

^a Average value of five runs of mass deacidification treatment using the CSC Book SaverTM process

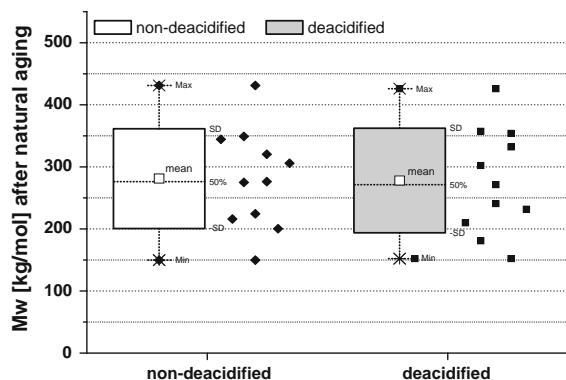


Fig. 4 Mw data box plot of books ($N = 11$) deacidified from 1994 to 1998 and their non-deacidified duplicates (published from 1892 to 1992). t test: two paired samples for means ($p < 0.05$) showed no significant difference between two sets of data

and is also decisive for whether long chains are oxidized or not and, if so, where the oxidation occurs (Scheme 1).

If the oxidized position leading to a chain splitting is located at an AGU at the very end or the very start of a cellulose chain, the degradation after alkaline treatment will not result in significant (or detectable) chain degradation, since only one or very few AGUs are cleaved and lost. This agrees with the fact that the molecular weight shows no significant decrease despite moderate losses in carbonyl content. The decrease in molecular weight is also only minor if already strongly degraded chains, i.e., short chains in the low molecular weight region, are affected by β -elimination. Also, their losses will not have a pronounced effect on the MWD.

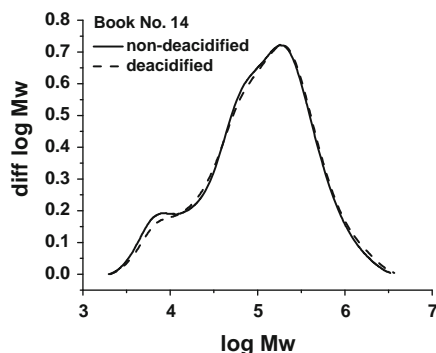


Table 3 summarizes the theoretical effect of β -elimination on the resulting number of keto/aldehyde groups (cf. Fig. 1) depending on the region of oxidation within a cellulose chain. Unless β -elimination occurs selectively due to the presence of a C-6 carbonyl located in the middle of the cellulose chain, the number of carbonyl groups will decrease or remain the same after β -elimination. Moreover, the extent of decrease strongly depends on the position of the carbonyl group along the cellulose chain. A significant decrease in the molecular weight is mainly accompanied by either a small loss of or even an increase in carbonyl groups. A stable value of the molecular weight always leads to a decrease in the carbonyl groups.

In the oxidized model pulps, we observed both a strong decrease in Mw and a decrease in carbonyl groups. In the naturally-aged papers after deacidification, a slight but significant reduction in along-chain carbonyl groups was seen, whereas the molecular weight remained stable. Based on this observation, we can state that, in model pulps, oxidation occurs largely along the chain, and also (or mainly) in the central parts. Under natural aging conditions, however, the chain ends are preferentially oxidized compared to positions in the middle region of a chain. This would also agree with the fact that chain ends are located in less ordered and thus more accessible areas compared to positions in the central parts of a large macromolecule, according to the fringed micelle model.

In addition to these conclusions, we can address the region of oxidation relative to the MWD, i.e., the question of whether high Mw areas or low Mw areas

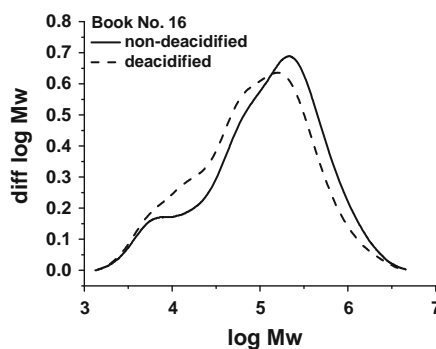


Fig. 5 Molecular weight distribution (MWD) of two sample sets of deacidified books and their non-deacidified duplicates. *Left* Example with only little alteration of the distribution (the book was published in 1960 and the deacidified issue treated in 1996 with the PapersaveTM process). *Right* Example with a

significant shift of MWD in the higher molecular weight region towards lower molecular weight (the book was published in 1970 and the deacidified issue treated in 1998 with the PapersaveTM process)

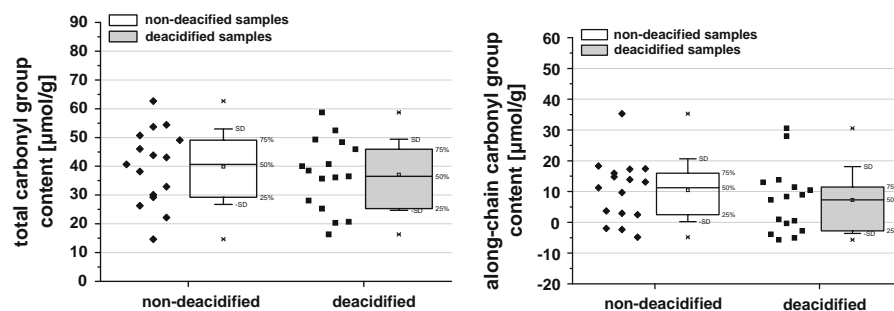
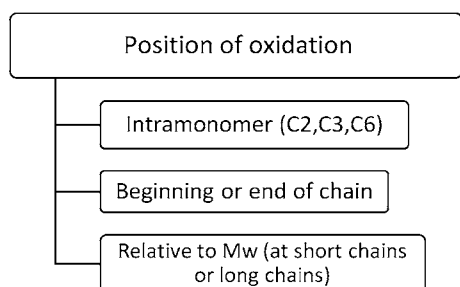


Fig. 6 Comparison of the content of carbonyl groups between non-deacidified and deacidified samples (only Papersave™ treated books are included, and coated papers No. 13N and D and No. BN and D are excluded). *Left* Total carbonyl group contents. *t* test: paired two-sample for means ($p < 0.05$) showed no significant difference between two sets of values. *Right*

Along-chain carbonyl group contents. *t* test: paired two-sample for means ($p < 0.05$) showed a significant difference between two sets of values. Along-chain carbonyl content is calculated from REG content estimated from Mn and measured total carbonyl group content. It provides a good estimation of its trend within the given sample sets, but not absolute correct values



Scheme 1 Different possibilities for oxidation within the chemical cellulose hierarchy, leading to different possible effects after β -elimination

are preferentially affected by the natural aging processes versus the artificially aged (oxidized) model. In Fig. 7, the percentage of total carbonyls in different regions of the MWD for the model pulp and one naturally-aged book paper are compared. Both have a similar overall MWD and starting carbonyl

content. In general, the degree of oxidation of paper and pulp is higher in the low Mw region. If β -elimination occurs in that region, the molecular weight is less strongly affected. About 52 % of all carbonyls are located in the region below DP 60 (9.700 g/mol) in the naturally-aged sample, while for the model pulp only 38 % are present in the same area. Thus, about 10 % more carbonyls are located in the bulk part between DP 200 and DP 2000, where β -elimination will have a stronger effect on Mw. This trend stays the same when averaging the values for all books investigated: > DP100: 56.0 %; DP100-DP200: 13.9 %; DP 200-DP2000: 25.5 %; DP > 2000: 4.5 % (N = 23, excluding coated papers).

From the data presented, a higher degree of oxidation at lower molecular weight regions was evident in the naturally-aged papers.

For mass deacidification, the observed behavior is “good news.” Although β -elimination can be detected

Table 3 Theoretical number of additional carbonyl groups (REG, keto, aldehyde) formed in the polymeric part of cellulose after β -elimination at different positions, according to Fig. 1, and the resulting effect on molecular weight

Oxidation in AGU before β -elimination	Number of C = O groups after β -elimination	Molecular weight (Mw) after β -elimination
C6 @ middle of chain	+1	Reduced significantly
C6 @ red. chain end	−1	Not reduced significantly
C6 @ non red. chain end	±0	Not reduced significantly
C3 @ middle of chain	−1	Reduced significantly
C3 @ red. chain end	−2	Not reduced significantly
C3 @ non red. chain end	−1	Not reduced significantly
C2 @ middle of chain	±0	Reduced significantly
C2 @ red. chain end	−1	Not reduced significantly
C2 @ non red. chain end	−1	Not reduced significantly

Fig. 7 Distribution of carbonyl groups within different areas of the MWD of an example book (No. 18N) and an oxidized model pulp. Total carbonyl group contents were 53.7 $\mu\text{mol/g}$ for No. 18N and 45.9 $\mu\text{mol/g}$ for the oxidized model pulp. Pie charts show percentages of total carbonyls in the respective DP regions, with similar MWD

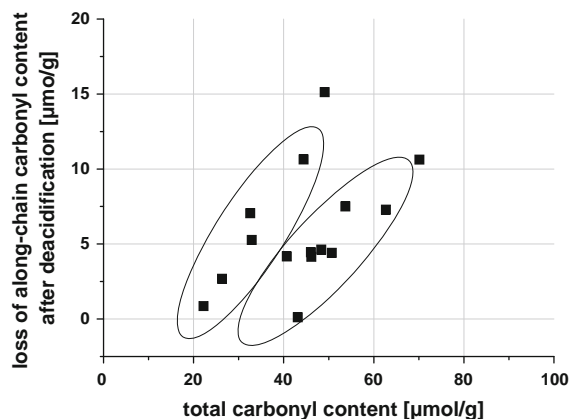
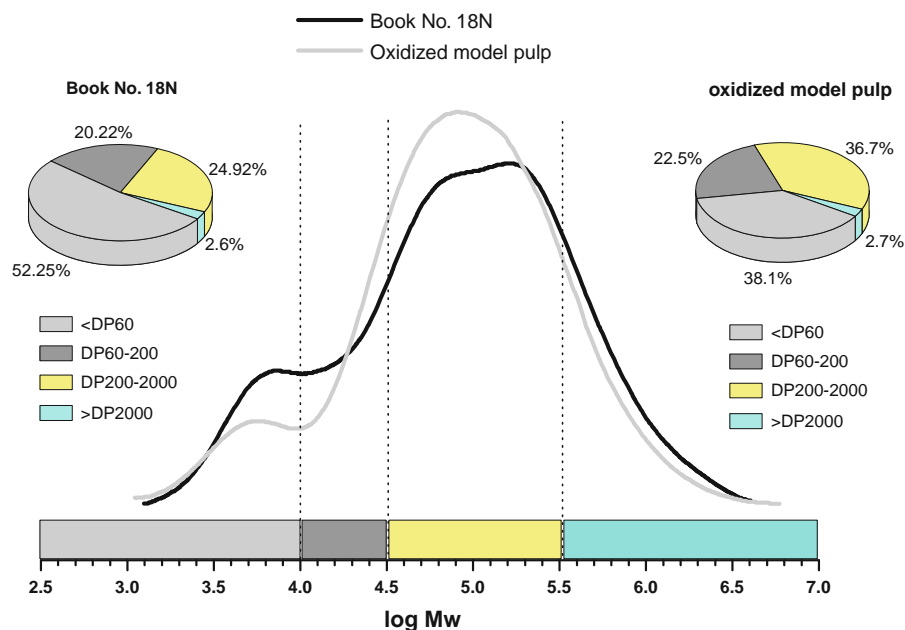


Fig. 8 Total carbonyl group contents of non-deacidified papers versus loss of along-chain carbonyl group contents after deacidification

with a sensitive method such as carbonyl determination according to the CCOA method, no damage to cellulose integrity is caused by the introduction of alkaline compounds in the mass deacidification treatment.

Malesic et al. (2002) investigated the effect of alkaline conditions on historic rag papers and found a similar behavior to that described above; the impact of a high pH on the cellulose DP was found to be rather low. In the present study, indications of β -elimination occurring during mass deacidification were only

detected in terms of a decrease in non-REG carbonyls, but not in terms of reduced molecular weight. The loss of along-chain carbonyl groups after deacidification versus the total carbonyl group content of non-deacidified papers is given in Fig. 8. There is only a very rough correlation between the initial carbonyl content and the loss of along-chain carbonyl content, showing a greater loss of along-chain carbonyls with higher values of the initial oxidized group contents. Since quite different types of library books were compared, we did not expect a straightforward, good correlation. From the behavior of carbonyls in combination with the data of the molecular weight, we can state that the residual carbonyls are very likely present in regions where their removal does not pose a risk for cellulose integrity.

Conclusion

The applied method of carbonyl detection and recording of the molecular weight can be used to get a deeper insight into natural aging and processes occurring upon mass deacidification. A significant degradation of cellulose due to β -elimination was found in the case of oxidized model pulps after mass deacidification depending on the overall content of total carbonyl groups. However, real book papers that had been

oxidized in the course of natural aging were found to be resistant to the treatment, showing no sign of significant chain cleavage induced by the alkaline conditions of mass deacidification. This different behavior can be explained by different sites of oxidation along the cellulose chains and within the AGU. While chemical oxidation affected the bulk material to a larger extent, natural aging showed oxidized functionalities predominantly at shorter chains. The observed decrease in keto and aldehyde groups other than the reducing ends is attributed to a preferred oxidation at chain ends. According to the data presented, it can be concluded that β -elimination is not a threat in the mass deacidification of naturally-aged book papers.

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Paper IV

**The influence of the
alkaline reserve on the
aging behavior of book
papers**

Cellulose, vol. 20, pp. 1989-2001.

The influence of alkaline reserve on the aging behavior of book papers

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Abstract Degradation of cellulose under alkaline conditions is involved either involuntarily or deliberately in many different cellulose processing steps, such as pulping, bleaching, or aging within the viscose process, and the underlying chemistry has been the topic of numerous studies. When it comes to aging under alkaline conditions—either natural or accelerated (artificial)—the degradation processes are by far less investigated and understood. A prominent example of moderately alkaline cellulosic material is deacidified book paper from libraries which had undergone a mass-deacidification treatment. We studied their aging behavior under accelerated conditions in comparison to non-deacidified duplicates in order to better understand how the alkaline reserve, which was introduced by the deacidification treatment, affects the stability of the books on the long run. GPC analysis of cellulose and determination of carbonyl functionalities were performed, which were critical parameters to achieve a deeper insight into hydrolytic and oxidative changes of cellulose structure upon deacidification treatment and subsequent aging. Also, model book papers impregnated with different amounts of alkaline reserve were used to support the findings from the original book samples. Hydrolytic degradation

rates of the original book papers were significantly reduced after mass deacidification compared to the non-deacidified duplicates. The beneficial effect of mass deacidification on cellulose stability was found to be strongly related to the amount of alkaline reserve deposited, independent of varying parameters of book papers. Although some indication of alkali-induced β -elimination was found (a minor decrease of the along-chain carbonyl content in the original deacidified book papers during aging), it did not occur to an extent that significantly influenced the molar mass of cellulose. The beneficial effect of retarded hydrolytic degradation by mass deacidification thus clearly outweighed possible negative alkalinity effects of the deposited alkaline reserve.

Keywords Paper · Historic paper · Mass deacidification · Accelerated aging · Alkaline reserve · Alkaline cellulose · β -Elimination · Oxidation · Carbonyl groups · Molecular weight · Cellulose degradation

Introduction

Most papers produced between 1850 and 1980 contain sizing agents based on alum and rosin, which over time generate considerable amounts of acids that are able to severely affect the integrity of the cellulose matrix. This acidification threatens whole stocks of libraries and museums, and requires remedies that are

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able to cope with bulk amounts of printed matter. The concept of mass-deacidification treatments of paper has been introduced to the conservation community in the late 1930s by Barrow, and already then it was stated that a certain amount of alkalinity, the so-called “alkaline reserve” is crucial to remain in the paper in order to neutralize acids that newly form over time (Roggia 2001). At about the same time, Hanson (1939) proposed a more specific amount of alkaline reserve for good paper permanence, observing excellent paper stability of historic rag papers that contained 2 % of calcium carbonate (0.4 mol/kg of alkaline reserve) at least. Based on the historical evidence as well as the technical development of appropriate methods, mass deacidification has now been applied to library objects for several decades aiming at neutralization of acid existing in paper and depositing an alkaline reserve as proposed some 80 years ago. Unlike alkaline treatments used in different pulp processing methods, the mass deacidification treatment is carried out under rather ‘mild’ alkaline conditions: it deals with pre-oxidized cellulose from aged papers which would severely suffer in a more harsh alkaline environment. The resulting pH of the deacidified book papers mainly ranges between 7 and 9 (Reist 2006; Ahn et al. 2011). Details of mass deacidification processes are available in numerous references and will not be further discussed here (Porck 1996; Blüher and Vogelsanger 2001; Banik 2005; Grossenbacher 2006; Gerlach 2006; Porck 2006; Andres et al. 2008; Stumpf 2006; Baty et al. 2010; Library of Congress 2011).

Our previous study established that the risk of chain scission by β -elimination reactions in naturally oxidized cellulose as a consequence of mass deacidification was rather insignificant, thanks to the characteristic distribution of carbonyl groups in cellulose of the naturally-aged papers (Ahn et al. 2012b). Although a direct damage risk of the treatment to the original book papers was shown to be negligible, the history of mass deacidification starting in the mid 1990s has been too short to reliably assure a positive long-term effect of the treatment. We detected neither a stabilization nor a degradation of deacidified papers that were naturally aged for 10–14 years after mass deacidification. Thus some important questions still remain: is it worth carrying on with mass deacidification of books from the financial and technical viewpoints? Can any adverse effects occur in the cellulose structure during

aging under alkaline conditions which might threaten the beneficial concepts of deacidification and deposition of alkaline reserves?

Once successfully treated by any variant of mass deacidification processes, book papers should be no longer acidic and, if at all, should undergo degradation pathways different from those of non-deacidified, i.e. still acidic, paper. While acid hydrolysis is dominant in degradation of acidic paper, the degradation mechanisms of the deacidified paper are still not well understood. Acid-triggered degradation is still possible locally in deacidified material, depending on how efficiently and how homogeneously alkaline earth carbonates or hydroxides are distributed within the paper and how they are able to react with acids formed in the process of natural aging of cellulose and hemicelluloses. In addition, β -elimination under alkaline conditions can produce additional acids according to several reaction mechanisms (Lewin 1997; Lai 2001; Potthast 2006). Also a radical-triggered reaction in alkaline environment as originally proposed by Entwistle et al. (1949) cannot be completely ruled out in the course of aging of deacidified papers. Since transition metal ions are generally present in paper, e.g. 4–77 ppm of Cu in machine-made papers (Praskiewicz and Subt quoted by Williams et al. 1977), they may catalyze such autoxidation reactions. Arney et al. (1979) showed that atmospheric oxidation of cellulose increased after deacidification. Hydroxyl radical formation in the deacidified model papers during accelerated aging was also reported (Kolar et al. 2001). Autoxidative degradation of cellulose will lead to formation of carbonyl groups, which generate in turn ‘hot spots’ for β -elimination under alkaline conditions (Fengel and Wegener 1984; Kolar 1997; Lai 2001). Hence, it is certainly valuable to better understand aging of cellulose in deacidified paper at the molecular level, in particular after a prolonged aging period in order to determine any long-term effects.

In this paper, sustainability of mass deacidification with regard to cellulose stability will be discussed, applying accelerated aging to original book samples and especially assessing the amount of alkaline reserve introduced. The degradation mechanism of deacidified book papers during accelerated aging is addressed analyzing oxidative functionalities as well as molecular weight of cellulose in direct comparison with original, non-deacidified duplicates. In addition to the original book papers, two different model book

papers and a reference paper were analyzed with regard to their aging behavior with different amounts of alkaline reserve, which complements the findings from original book papers.

Methods and materials

Sample preparation for GPC

CCOA (Carbazole-9-Carbonyl-Oxy-Amine) labeling of carbonyl groups and FDAM (9H-fluoren-2-yl-diazomethane) labeling of carboxyl groups were performed as described earlier (Röhring et al. 2002a, b; Potthast et al. 2003; Bohrn et al. 2006). The standard preparation method was applied. In the case of library books, to reduce any variation due to an inhomogeneous deacidification treatment, about 100 mg of dry sample were disintegrated, and 25 mg of wet sample were used for labeling. After labeling, dissolution in *N,N*-dimethylacetamide/lithium chloride 9 % (w/v) (DMAc/LiCl) was achieved via solvent exchange at room temperature. Measurements were performed with a GPC-Fluorescence-MALLS-RI system that yields molecular weight (MW) and molecular weight distribution (MWD) in addition to the content of oxidized groups in relation to the MW. Samples to be compared were prepared and measured in a same batch with a reference paper.

GPC conditions

The GPC system used consists of a fluorescence detector TSP FL2000 for monitoring the CCOA label, a multiple-angle laser light scattering detector (MALLS) (Wyatt Dawn DSP) with argon ion laser ($\lambda_0 = 488$ nm), and a refractive index detector (Shodex RI-71). Four serial GPC columns (Polymer LaboratoriesTM (current VarianTM/AgilentTM) PLgel mixed ALS, 20 μ m, 7.5 \times 300 mm) were used as the stationary phase. Degasser (Dionex DG-2410), auto-sampler (HP 1100), pulse damper pump (Kontron pump 420), and column oven (Gynkotek STH 585) were parts of the system.

Operating conditions: 1.00 ml/min flow rate, 100 μ l injection volume, 45 min run time, $\lambda_{\text{ex}} = 290$ nm and $\lambda_{\text{em}} = 340$ nm for fluorescence detection of the CCOA label, $\lambda_{\text{ex}} = 280$ nm and $\lambda_{\text{em}} = 312$ nm for fluorescence detection of the FDAM label. DMAc/

LiCl (0.9 %, w/v) after filtering through a 0.02 μ m filter was used as eluant.

Data evaluation was performed with standard Chromeleon, Astra 4.73, and GRAMS/32 software. From the total amount of carbonyl groups obtained by GPC, the theoretical amount of reducing end groups (REGs) were calculated from M_n (number-average molar mass) on the assumption that determination of M_n is correct and that no REGs are converted to acids by oxidation (Potthast et al. 2008). The value of along-chain carbonyl content was calculated according to the following equation: Along-chain carbonyl content ($\mu\text{mol/g}$) = total carbonyl content ($\mu\text{mol/g}$)—REGs ($\mu\text{mol/g}$).

According to results from standard pulps ($N > 500$), the standard deviation for carbonyl groups is below 5 %, for M_w about 5 %, and for M_n around 10 %.

Sample book papers and mass deacidification treatment

Twenty five deacidified books were selected from the stocks of the German National Library in Leipzig and the Berlin State Library in 2009. Exact duplicates were obtained from second-hand markets in central Europe. Both sets of books—one deacidified, the other not—were analyzed in parallel. Three different mass deacidification processes had been applied; one book was treated with a dry system, the LibertecTM process, and 24 books were treated with two different non-aqueous immersion systems, the CSC Book SaverTM process and the PapersaveTM process. Table 1 contains the list of samples. Additional information (e.g. publication year) is available in Ahn et al. (2012b). N and D in sample description denote ‘non-deacidified’ and ‘deacidified’ specimens, respectively.

Whatman filter paper no. 1 served as the reference paper containing almost pure α -cellulose without sizing or fillers.

Accelerated aging

A dynamic accelerated aging method in a closed system was applied to the original book samples in this study, attempting to simulate both degradation rate and natural aging conditions of books. Book samples and reference papers were placed in a paper stack and wrapped with aluminum foil several times. Conditions

Table 1 Ratio of ω_{DP} non-deacidified and ω_{DP} deacidified, and surface pH of deacidified paper for each sample set number

Sample no.	Ratio of ω_{DP} non-deacidified to ω_{DP} deacidified	Surface pH for deacidified paper	Deacidification process	Remarks
1	3.0	8.7	Papersave	
2	2.5	7.6	Papersave	
3	1.1	5.9	CSC Book Saver	
4	1.2	8.8	Libertec	
5	3.1	8.2	Papersave	
6	1.2	7.5	CSC Book Saver	
8	3.3	9.2	Papersave	
10	7.8	8.8	Papersave	
11	7.1	8.2	Papersave	
13	0.8	7.5	Papersave	Coated paper
14	2.2	9.1	Papersave	
15	3.4	9.3	Papersave	
16	3.4	9.0	Papersave	
17	2.2	8.7	Papersave	
18	3.2	8.6	Papersave	
19	4.1	7.5	Papersave	
20	3.3	8.0	Papersave	
21	3.3	9.0	Papersave	
22	14.7	8.8	Papersave	
23	1.1	6.6	CSC Book Saver	
24	−17.7 ^a	9.1	CSC Book Saver	CaCO ₃ contained before deacidification
25	1.4	8.4	CSC Book Saver	
26	2.2	6.0	CSC Book Saver	
A	2.5	9.1	Papersave	
B	1.0	4.5	Papersave	Coated paper

^a The negative value resulted from ω_{DP} of deacidified paper—24D (−0.01), showing no Mw loss within the error of measurement

of accelerated aging were the following: cycling between 45 and 80 °C every 6 h without humidity control during the first 8 weeks and cycling between 20 and 80 °C every 6 h with 50 % of relative humidity for the next 7 weeks. Thus, all samples had been aged for 15 weeks in total. For the kinetic study, some of samples were aged for 14, 70, and 105 days.

Determination of alkaline reserve and surface pH

The alkaline reserve was determined by the standard titration method according to ISO 287:1985 and modified ISO 10716:1994. Due to colour interference of the pH indicator in solution, pH measurement was carried out with a pH electrode (Mettler Toledo InLab® Easy BNC, pH 0–14, 0–80 °C), and a titration curve was recorded. The curve served for determination of the amount of alkaline reserve (mol/kg), and

the end point was determined at pH 7. Surface pH was measured according to TAPPI T529 om-88 using a flat combination pH electrode (Mettler Toledo InLab® Surface, pH 1–11, 0–50 °C) and a pH meter (Mettler Toledo SevenEasy pH meter).

Impregnation of alkaline reserves into model book papers and their accelerated aging

Two book papers were selected and treated with various concentrations of magnesium propoxycarbonate deacidification reagent (CSC Booksaver™ by Conservacion de Sustratos Celulosicos S.L., Spain) to create different amounts of alkaline reserve in the papers. The structure of this reagent was previously elucidated (Henniges et al. 2012). Solutions of 5, 10, 20, and 40 % (v/v) in 1-propanol were sprayed on the front and the back of each book paper. Excess solution

was removed with placing them between blotting papers. Samples were dried and stored under ambient conditions until artificial aging started. Whatman paper no. 1, as a reference, was also treated in a same way together with the model book papers. The samples were aged in a chamber at 80 °C and 65 % relative humidity for approx. 43 days (1029 h) according to ISO 5630-3:1996. Samples were not completely sealed (like the original book samples), but still stacked to simulate a book during accelerated aging.

Results and discussion

Influence of accelerated aging on the reference paper

Introductorily, we are well aware of the fact that accelerated aging may not entirely reflect the natural aging occurring over many years under natural climate conditions. However, in order to judge the stability of an organic material or the stability improvement obtained after a special conservation treatment, accelerated aging is still an important tool for relative comparison (Porck 2000). The applied accelerated aging conditions are known to be close to the situation of book papers collecting degradation products between the stacks of paper (Begin and Kaminska 2002; Shahani 1994). The uncertainty of artificial aging exactly reflecting natural aging will be somewhat diminished in this study by the fact that the data are quasi relative, i.e. obtained by comparison of the two sample sets (deacidified and non-deacidified) that underwent exactly the same accelerated aging conditions.

The results from the reference paper (Whatman paper) will be discussed first to understand how the accelerated aging procedure affected cellulose degradation. The reference paper can give information about pure cellulose degradation without any influence of other additives during the aging. As seen in Fig. 1, left, during the course of aging M_w and M_n of the reference paper decreased according to a first-order rate law. Carbonyl groups increased accordingly, almost exclusively due to the increase in reducing end groups (Fig. 1, right). This behavior nicely proves the intended hydrolytic nature of cellulose degradation during the type of accelerated aging chosen. Looking at the along-chain carbonyl

content and the uronic acid content during the course of aging (Fig. 1, right), it was evident that novel oxidative functionalities due to oxidation are not generated to a significant level: the newly formed REGs originate from the hydrolytically cleaved chain fragments. Therefore, this aging method turned out to be ideal in order to simulate a hydrolytic degradation mechanism.

Figure 2 gives a schematic overview of the fundamental reactions during aging of book papers after mass deacidification. These processes highly depend on the state of the original paper before deacidification and on how much and how homogeneously deacidification occurred. Before mass deacidification the papers are acidic, after the process and during aging they have a moderately alkaline pH (below 10.5). β -Elimination starting from oxidized functionalities present in naturally aged papers, a fast process, already occurs during mass deacidification (cf. Fig. 2a).

The alkaline reserve introduced during mass deacidification is often not distributed homogeneously. Consequently, this may still lead to local acidic hydrolysis in an overall alkaline paper (cf. Fig. 2c). Furthermore, a slow oxidation in the presence of oxygen during subsequent aging followed by a fast β -elimination at the newly generated oxidized positions can take place. This reaction (Fig. 2b) can be considered slow compared to the other processes.

Influence of accelerated aging on original book papers—molar mass

Cellulose degradation during accelerated aging is often characterized by the ratio of the number of chain scissions and the starting DP_0 ($1/DP_t - 1/DP_0$) versus time of accelerated aging applying a simplified Ekenstam equation (Ekenstam 1936 as quoted by Sixta et al. 2006). Application of the inverse DP in the equation has originated from results of viscosity determinations (Fellers et al. 1986).

However, historic book samples represent a more complicated type of material as they exhibit various stages of natural aging, not to mention the different paper-making parameters according to which they were produced. Consequently, simple application of the Ekenstam equation to all historic samples seems at least questionable. Especially for relatively short cellulose chains, i.e. lower starting DP_0 , the Ekenstam

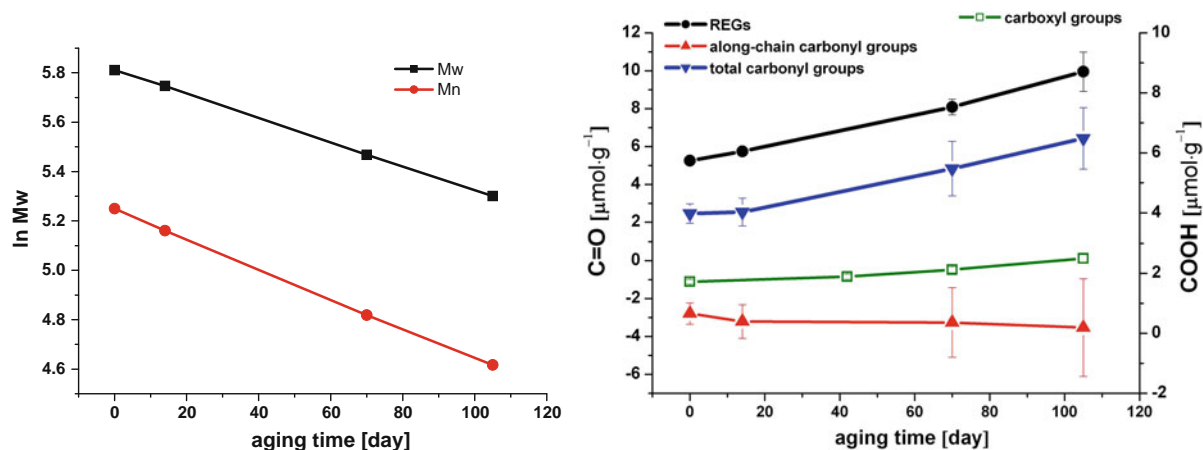
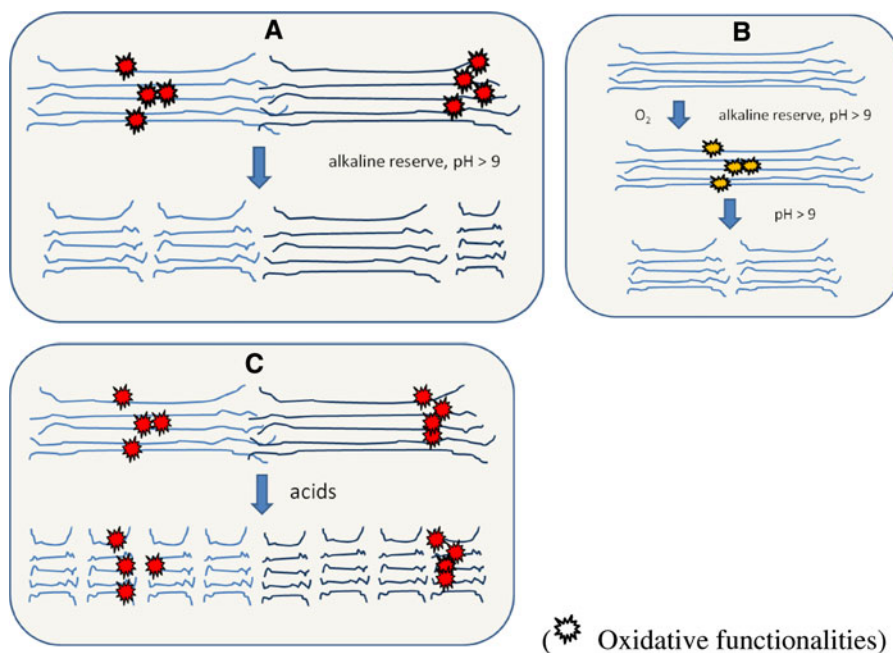


Fig. 1 Reference paper during accelerated aging. *Left* Change of Mw and Mn. *Right* Change of carbonyl and carboxyl groups. Average values of three measurements are presented except for

carboxyl group content. Error bars represent standard deviation. Otherwise, 5 % of error was assumed

Fig. 2 Schematic of cellulose degradation processes during aging of deacidified paper. **a** β -elimination (oxidative peeling); **b** Oxidation followed by β -elimination; **c** Acidic hydrolysis due to acids that alkaline compounds failed to neutralize



equation always results in higher hydrolysis rates compared to long cellulose chains with the same number of chain scissions. Eventually, this will falsely lead to a relatively higher efficiency of deacidification for papers with high DP. Therefore, the percentage DP loss was applied in our study. Introduced by Ding and Wang (2008a, b) and defined as degree of degradation, ω_{DP} , equal to $1 - DP_t / DP_0$ has proved to be a reliable measure of cellulose degradation for special cases, such as aging in closed vessels,

which is close to our accelerated aging approach in sealed stacks.

Figure 3 illustrates the rates of cellulose degradation of three different sample sets characterized by ω_{DP} ($1 - DP_t / DP_0$) versus time of the accelerated aging. Samples 1D and 8D, which had been successfully deacidified resulting in pH 8.7 and pH 9.2, respectively, clearly showed a reduced rate of degradation compared to their non-deacidified counterparts 1N and 8N. For the initial rate a linear fitting based on

first-order reaction kinetics provided rates reduced by a factor of 3.0 and 3.2, respectively, for 1D and 8D, relative to 1N and 8N. Acidic hydrolysis was evidently efficiently suppressed due to the presence of the alkaline reserve acting as a barrier against acidic attack as expected for the deacidified papers. As acids were detected even in the deacidified paper during aging (Shahani and Harrison 2002; Doering 2007), the efficiency of alkaline reserve as a preventive constituent from acidic hydrolysis in paper depends on various parameters of alkaline reserve, such as which alkali compound is formed, where and how much is left in the paper, and in particular whether it is homogeneously distributed or not.

Sample 3D in Fig. 3 represents an example of an insufficient quantity of alkaline reserve. Sample 3N was an extremely acidic paper requiring 0.16 mol/kg of alkalinity for neutralization. However, 3D contained still “minus 0.03 mol/kg” of alkaline reserve, i.e. the paper was still acidic even after mass deacidification, and the alkalinity applied was thus not sufficient for neutralization. This resulted in only a slight decrease of the degradation rate in 3D during aging compared to the non-deacidified 3N. In addition, sample 3N was extremely fragile and brittle with a DP < 500, which is presumably close to the level-off DP (LODP). In this case, improvement of cellulose stability with a deacidification treatment is generally limited.

In a case similar to sample 3D, sample 4D deacidified with the LibertecTM process which treats

each book by a dry air stream of micron-sized magnesium oxide gained very little benefit from this treatment. Although the overall alkaline reserve of 4D was 0.08 mol/kg, the majority of alkaline reserve was located on the surface of paper, but not in the bulk paper matrix, and the sizes and shapes of the MgO particles were coarse and irregular (Ahn et al. 2012a) resulting in an ω_{DP} of 0.30 after aging (cf. ω_{DP} of 0.36 for 4N). Therefore, the treatment failed to deposit an efficient alkaline reserve being finely and homogeneously distributed throughout the paper matrix as well as on the surface (Ramin et al. 2009; Ahn et al. 2012a). The rate of cellulose degradation of sample 4D was, in spite of a surface pH of 8.8, almost identical to its non-treated duplicate (4N), which indicated an inefficient contribution of MgO particles in overall deacidification.

The histogram of Mw loss (%) of all original book samples after accelerated aging is given in Fig. 4, left. It was evident that deacidified samples were degraded much less compared to their non-deacidified duplicates after aging. The extent of reduction of the Mw loss (%) greatly depended on the original conditions of sample papers and the type of mass deacidification process as mentioned above.

As obvious from Table 1, the PapersaveTM process resulted in a relatively higher ratio of ω_{DP} non-deacidified/ ω_{DP} deacidified, indicating a larger benefit from the treatment compared to LibertecTM and CSC Book SaverTM. According to our previous studies on surface pH and alkaline reserve with an extended number of samples (Ahn et al. 2011, 2012a), an insufficient amount of alkaline reserve is responsible for the lower cellulose stability of the CSC Book SaverTM treatment. A relatively small benefit from the LibertecTM process was elucidated above. Therefore, generally, the samples having undergone a successful deacidification treatment (sufficient amount of alkaline reserve homogeneously distributed over the whole paper cross-section) profited from largely improved cellulose stability.

This finding led to the first conclusion that alkaline reserves, even of sufficient amounts, were only active and long-term beneficial if evenly distributed and freely “accessible” for acids present. Secondly, for properly dispersed alkaline reserves their amount left after mass deacidification was one of the most important factors to reduce the hydrolytic degradation of cellulose. After accelerated aging, ω_{DP} correlated

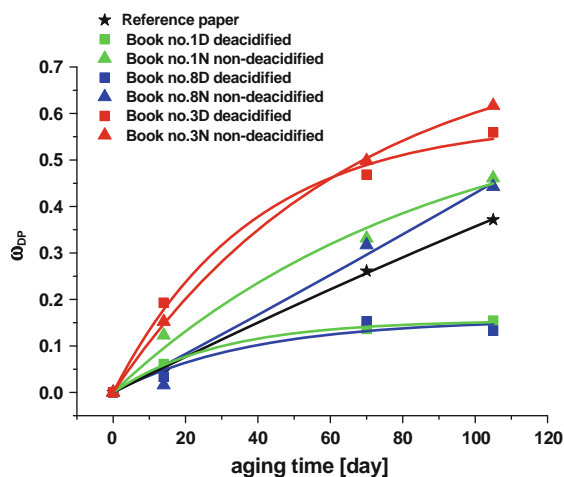


Fig. 3 Rates of cellulose degradation of deacidified books and their non-deacidified duplicates, plotted as accumulated percentage DPw loss. Samples 1D and 8D were well deacidified while specimen 3D was not

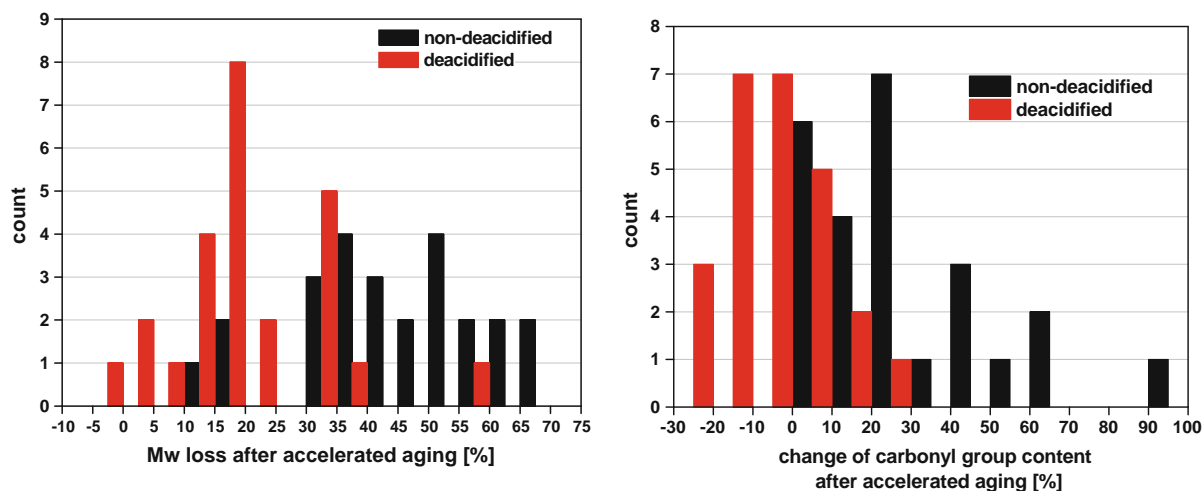


Fig. 4 Left Histogram of Mw loss (%) of samples after accelerated aging. Right Histogram of change (%) of the total carbonyl group content after accelerated aging

with the amount of alkaline reserve determined by the standard method of titration (Fig. 5), indicating a higher beneficial effect with higher amounts of alkali. Considering all different parameters of the book papers, such as deacidification conditions, paper making parameters, oxidative functionalities and their contents, age, storage conditions—and probably others –, the alkaline reserve clearly was the decisive factor for cellulose stability in all kinds of book papers. The data imply that a certain threshold amount of alkaline reserve (about 0.4–0.5 mol/kg according to the accelerated conditions) is to be deposited in the paper for the deacidification treatment to be sufficiently efficient. The currently proposed minimum amount (Hofmann and Wiesner 2011) of 0.12 mol/kg alkaline reserve must be adjusted accordingly.

An important question is whether any adverse effects of the alkaline reserve on cellulose integrity play a role or not. If alkaline degradation occurs to a major extent and causes severe chain scission during aging, there would be no such correlation between alkaline reserve and cellulose stabilization observed over such a large range of alkaline reserve, especially not in the range of higher alkaline reserves (Fig. 5). The correlation observed was roughly linear from the acidic region to the alkaline region ($R^2 = 0.71092$). According to the data from Mw of sample papers the major cellulose degradation mechanism was hydrolysis and was hence directly affected by alkaline reserve. Alkali amounts higher than 0.5 mol/kg were not often found in the original book papers analyzed and are not

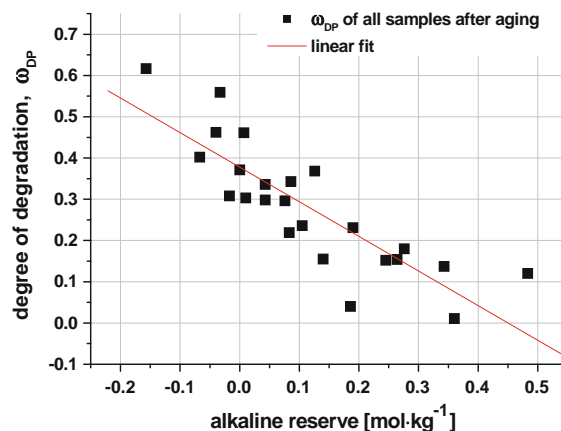


Fig. 5 Amount of alkaline reserve of books determined by titration versus degree of degradation (ω_{DP}) after accelerated aging ($R^2 = 0.71092$)

discussed here, but will be covered later in the section on model book papers. In order to judge base-induced degradation reaction on cellulose (cf. Fig. 2) the molar mass in combination with reactive groups, i.e. carbonyls, need to be considered. We applied the CCOA fluorescence-labeling method (Röhring et al. 2002a, b; Potthast et al. 2003) for this purpose.

Influence of accelerated aging on original book papers—carbonyl groups

Results of total carbonyl group contents are summarized in Fig. 4, right, showing the percentage change

of total carbonyl groups after aging. In the majority of deacidified samples, the total carbonyl content either decreased or did not change after accelerated aging. In contrary, all non-deacidified samples showed an increase in carbonyls, mainly due to generation of new reducing end groups (REGs) due to hydrolysis.

A more in-depth evaluation showed how carbonyl groups of the individual samples responded to the conditions of accelerated aging, displayed here by means of the example books no. 1 and no. 8. In Fig. 6, upper, sample 8N, the non-deacidified paper showed a rapid increase in total carbonyl groups as well as in REGs. In an ideal case of pure hydrolytic cellulose degradation, all newly generated carbonyl groups are contributed by REGs from hydrolytic chain scission as proposed by Whitmore and Bogaard (1994) (dotted line in Fig. 6, lower).

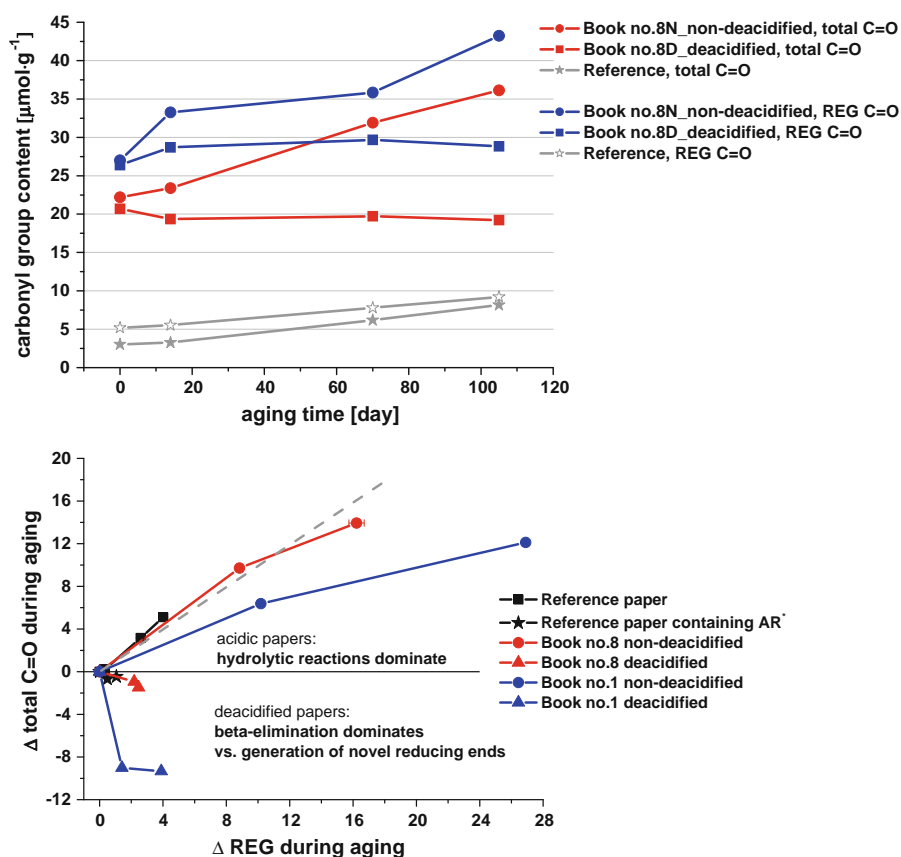
Sample 8N, non-deacidified paper in Fig. 6, in principle follows the idealized hydrolytic degradation route. In case of sample 1N, REGs increase remarkably, again overruled by hydrolytic reaction although

consumption of existing carbonyl groups by further oxidation seemed to occur at the same time.

After deacidification the hydrolytic reactions during aging were considerably slowed down and were not dominant anymore. Reactions such as β -elimination cause an overall decrease in carbonyl groups accompanied by a rather slow increase in reducing ends (cf. 1D and 8D in Fig. 6, lower).

In line with this finding is the slight, but significant decrease of the carbonyl group content observed already after deacidification without applying any accelerated aging (Ahn et al. 2012b), as well as in the cases of alkali cellulose (Potthast et al. 2006) and oxidized celluloses treated with sodium hydroxide (Bogaard and Whitmore 2001; Potthast et al. 2007). Considering the alkaline environment of the deacidified papers during aging, a higher consumption of the carbonyl group content compared to the non-deacidified papers can be attributed to β -elimination reaction that leads to loss of C-2, C-3 keto groups and C-6 aldehyde groups due to transformation into acids

Fig. 6 Upper Contents of the total carbonyl groups and the REGs of sample 8N and 8D during aging. Lower Aging behavior of deacidified papers and non-deacidified counterparts demonstrated by change of the total carbonyl group content versus change of the REG content (indicator of hydrolysis) (cf. Figure 3 for ω_{DP} data). Dotted line indicates an ideal pure hydrolytic degradation, i.e. $\Delta \text{REG} = \Delta \text{total C=O}$



according to benzylic acid rearrangements or retro-Claisen reactions (Lai 2001; Lewin 1997; Potthast 2006).

Looking at the along-chain keto/aldehyde contents of all samples, this finding is confirmed: the deacidified papers showed a relatively higher decrease in the along-chain carbonyl group content as compared to the non-deacidified papers (cf. Fig. 7). A statistically significant decrease of the along-chain carbonyl group content after aging was found only in the data groups of the deacidified papers (*t* test: paired two samples for means, $p < 0.1$, see Fig. 7).

As we confirmed β -elimination processes, it was important to assess to which extent they might occur. Several model studies described that adverse effects of deacidification treatment were reflected in DP or molar mass losses, especially when oxidized samples were treated (Kolar and Novak 1996; Bogaard and Whitmore 2001; Malesic et al. 2002; Stephens et al. 2009). Our Mw data showed the original book papers, which contained much higher carbonyl contents (around 40 $\mu\text{mol/g}$ on average) compared to the tested model papers or pulps in general, to be rather stable after mass deacidification. The amount of decreased along-chain carbonyl groups, which is the only evidence of β -elimination, correlates neither with Mw loss (%) ($R^2 = 0.1139$) nor with the initial content of carbonyl groups ($R^2 = 0.2694$). Therefore, the β -elimination we deduce from the slight decrease in the along-chain carbonyl content of the treated original book papers did not accompany severe chain

scission. The reasons for this behavior have already been discussed (Ahn et al. 2012b).

The mass deacidification treatments applied to the original book samples deposit only moderate amounts of alkaline reserve in paper. In order to better stimulate β -elimination reactions, model book papers with a higher alkaline reserve were investigated.

Model book papers with different amounts of alkaline reserve

Two different model papers from books and a reference paper, all impregnated different amounts of an alkaline reserve, were aged and their Mw and along-chain carbonyl groups were analyzed.

In general, the same trend in Mw loss (%) was ascertained as for the original book samples, i.e., a higher alkaline reserve lowered the Mw loss after aging in all model papers (Fig. 8, left). However, when it reached an alkaline reserve of more than 0.2 mol/kg, the extent of improvement of cellulose stability was different between model papers. Model book paper 1, which showed a higher initial total carbonyl content (Table 2) and a higher degradation rate compared to model book paper 2, exhibited a limited improvement even after applying about 0.2 mol/kg of alkaline reserve. On the other hand, in model book paper 2, alkaline reserves up to 0.6 mol/kg correlated linearly with improved cellulose stability during aging. For model book paper 1, a parallel degradation reaction seems to occur during aging cancelling out the beneficial effect of alkaline reserve when impregnation goes beyond 0.2 mol/kg. Looking at the change of along-chain carbonyl groups after aging, model book paper 1 was found to be much more sensitive to the amount of alkaline reserve, resulting in a relatively rapid decrease of along-chain carbonyl groups (Fig. 8, right). Decreasing along-chain carbonyl groups shows a more or less linear relationship to the amount of alkaline reserve and displays no direct correlation with Mw loss. This indicates that the model book paper 1, which is more sensitive to β -elimination, may have a lower threshold for the level of beneficial alkalinity.

However, no negative effect on Mw even beyond the threshold level seems to occur, since β -elimination takes place mostly at chain ends or short chains (Ahn et al. 2012b). Therefore, decreasing along-chain carbonyl group contents after aging do not necessarily

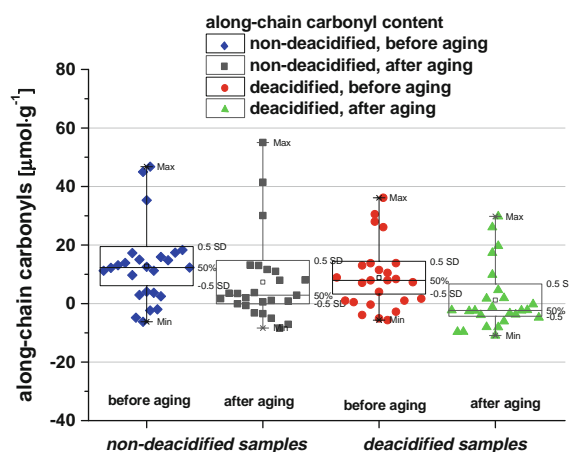


Fig. 7 Along-chain carbonyl group contents of non-deacidified samples and deacidified samples before and after accelerated aging

Fig. 8 *Left* Mw loss (%) of two model book papers and a reference paper with different amounts of alkaline reserve after accelerated aging. *Right* Difference of along-chain carbonyl groups of the same papers after accelerated aging. Data in an *ellipse*: untreated (non-deacidified) samples

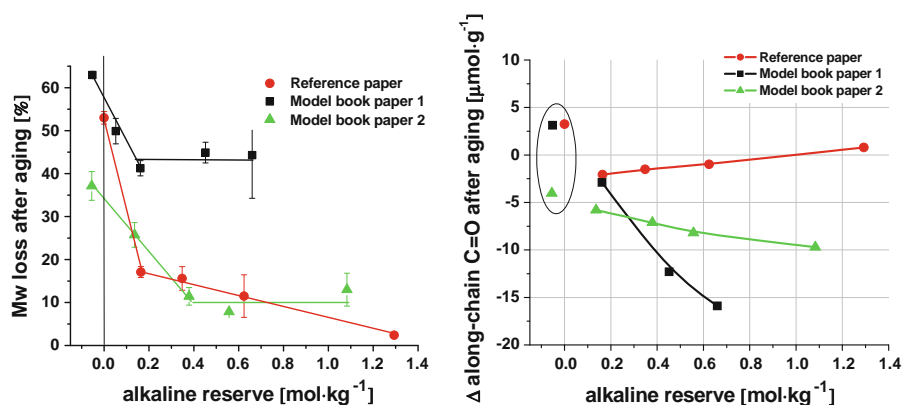


Table 2 Initial values of the model papers before aging

	Mw (kg/mol)	Total CO (μmol/g)	Year of publication
Reference paper	284.3±8.6	2.76±0.51	
Model book paper 1	255.4±23.1	28.00±0.34	1987
Model book paper 2	385.4±11.2	20.42±1.14	1968

mean that β -elimination occurred to an extent that negatively influences the beneficial effect of alkaline reserve. However, each book paper has a certain threshold of alkaline reserve, depending on the nature of the paper, from which β -elimination starts to progressively counteract the beneficial effect of the alkaline reserve.

Conclusions

Original book papers treated by a mass deacidification process and their non-deacidified duplicates were subject to accelerated aging and were subsequently comprehensively analyzed. Although the book papers contained a natural level of oxidative damage prior to the treatment, there was no evidence of severe cellulose chain scission induced by the alkaline environment during accelerated aging. Instead, cellulose degradation was significantly retarded in the deacidified papers thanks to alkaline reserve as compared to the non-deacidified papers. This beneficial effect of mass deacidification was found to be strongly related to the amount of alkaline reserve deposited after deacidification, independent of various other parameters of book papers. The correlation between the amount of alkaline reserve and degree of

degradation (ω_{DP}) was found to be linear over a long range from the acidic region to the mildly alkaline region.

Investigation of the carbonyl group contents after accelerated aging revealed that the original deacidified book papers showed reduced along-chain carbonyl contents after accelerated aging, which is a result of alkali-induced β -elimination processes. These β -eliminations, hence, have to be considered a side effect of mass deacidification. However, lowering the along-chain carbonyl contents as a sign of β -elimination was not strongly related to Mw loss in the original book samples. This further confirmed that the location of along-chain carbonyl groups induced by natural aging is rather at the chain ends than in the middle of cellulose chains as previously concluded (Ahn et al. 2012b)—only then a loss in along-chain carbonyls will not be accompanied by a severe loss in Mw. Furthermore, model book papers which were impregnated with increasing amounts of alkaline reserve exhibited an increasing loss of along-chain carbonyl groups. Also here the beneficial effect of mass deacidification is not negatively overcompensated. However, there is a certain threshold beyond which alkaline reserves do not improve cellulose stability further, but still lower along-chain carbonyl groups. Then a risk exists that β -elimination occurs to an extent that diminishes the beneficial stabilizing effect of alkaline reserves.

In conclusion, mass deacidification treatments applied to original book papers must reasonably be expected to contribute greatly to paper permanence.

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