Evaluation of Bookkeeper mass deacidification based on historical book papers

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Received: 14 December 2021 / Accepted: 30 May 2022 / Published online: 28 June 2022
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Abstract Bookkeeper, the most widely used deacidification process based on MgO particles, was systematically evaluated on two sets of nonvaluable historical paper samples. Established analytical methods, such as pH and alkaline reserve determination, were used, as well as SEM EDS analyses to evaluate the distribution of Mg-rich particles on the paper surface and in the cross-section of the paper. The degradation rate constants of untreated and deacidified paper samples after accelerated thermal degradation were calculated based on weight average molecular mass determination to evaluate the lifetime extension of paper. The efficiency factors determined after accelerated thermal degradation of untreated and treated paper showed that paper lifetime prolongation after Bookkeeper deacidification treatment is highly limited for most of the investigated paper samples. No correlation was found between the alkaline reserve content or the pH and the degradation rate constants of the deacidified paper samples, but the paper degradation rate correlated with the paper samples pH before deacidification treatment. SEM EDS analysis showed that Mg-rich particles remained on the paper surface, which explains the limited effectiveness of the treatment.
Graphical abstract

**EVALUATION OF MASS DEACIDIFICATION**

**ACIDIC HISTORICAL PAPER**

\[ \text{MgO dispersed particles} \]

**DEACIDIFIED HISTORICAL PAPER**

- increased pH value
- distribution of Mg-rich particles
  - surface
  - cross-section
  - alkaline reserve

**Keywords** Bookkeeper · Deacidification · Cellulose · Historical paper · Alkaline reserve · Efficiency factor

**Introduction**

The acidity of paper is a serious problem for many archival and library collections. It is generally agreed that the addition of aluminum sulfate (alum), which was used as a sizing agent in the final stages of paper-making from the mid-nineteenth century until the final decades of the twentieth century, is the main cause of paper acidity (Strlič and Kolar 2005). It is primarily alum that initiates hydrolytic reactions that produce adversely acting \( \text{H}_3\text{O}^+ \) ions (Jablonsky et al. 2020), which lower the pH of the paper and promote degradation by acid hydrolysis. The concentration of \( \text{H}_3\text{O}^+ \) ions in paper documents can be reduced and neutralized by immersion in various solutions or dispersions of alkaline agents in a treatment named deacidification (Baty et al. 2010; Hubbe et al. 2017; Lienardy and Van Damme 1990).

Tens of tons of books and archival material with acidic paper stored in the libraries and archives are treated every year worldwide by applying mass deacidification treatments to increase the overall lifetime of the supporting paper matrix by neutralizing acids present in the paper (Potthast and Ahn 2017). In addition to neutralization, most of the paper deacidification processes also provide an alkaline reserve to neutralize acids that may be introduced later, either generated within the paper itself or absorbed from its storage environment (Baty et al. 2010).

Large-scale operations apply the deacidification agent either as a solution or a dispersion in nonaqueous, largely inert solvents (Hubbe et al. 2017, 2018). Dispersion processes based on MgO particles, such as commercially available Bookkeeper (Preservation Technologies a) and ZfB2 (Zentrum für Bucherhaltung, ZFB:2. Massenentsäuerung.), are currently the most widely employed (Hubbe et al. 2017). During the treatment, the MgO particles are distributed throughout the book and dissolved within the paper fibers over time to form alkaline Mg-rich species and neutralize the acidity (Hubbe et al. 2017).

A recent evaluation of the ZfB2 process, introduced in Germany, was performed (Potthast and Ahn 2017), while no recent investigations have been carried out on Bookkeeper deacidification treatment, which is the most widely used deacidification process. A comprehensive study of its efficiency was conducted at the beginning of the 1990s (Buchanan et al. 1994), and its efficiency was evaluated during the PaperTreat project (Balažic et al. 2007) by Ramin et al. (2009) and the KnihaSK Consortium (Katuscak et al. 2012).

The evaluations, based on accelerated thermal degradation tests, have yielded a range of results for Bookkeeper deacidification treatment. Preservation Technologies B.V., the provider of the Bookkeeper deacidification treatment, claims that treatment by the Bookkeeper process should extend the usable life of paper-based materials by a factor of at least 3-5 times (Preservation Technologies b). The treated model papers retained their mechanical properties during accelerated thermal degradation for 2-4 times longer in comparison to untreated papers (Buchanan...
et al. 1994). Similar results were obtained by Balažic et al. (2007), who showed that Bookkeeper treatment would extend the usable life of paper by a factor of 3.3 ± 0.9, which also meets the Library of Congress standards, an important Bookkeeper user basic preservation requirement to extend the usable life of paper by a factor of over 3 (Library of Congress). In contrast, other results have shown that the treatment was less effective or even ineffective in increasing the mechanical permanence of the model paper containing groundwood pulp (Katuscak et al. 2012). In addition to the differences in the results of the efficiency of the treatment, the main drawback of the evaluations mentioned above is because the tests were carried out on a limited number of model paper samples, usually blank sheets of diverse paper types.

The survey of the printed monograph collection of approximately 125,000 books at the Slovenian National and University Library (NUL) was performed during the 6th Framework Programme EU project PaperTreat (Kolar et al. 2008) in 2006. A selection of 1000 books, printed between 1850 and 1990, was examined. The determination of paper pH values from the books showed that a significant decrease in pH from average values of 6.5 ± 1.0 to 4.0 ± 0.7 occurred in the 1870s, reflecting the change from gelatin to acid-rosin sizing technology. Since the 1940s, a gradual increase in the pH values of paper has been observed. The survey showed a dramatic condition of the collection, of which one-third were already in a severe state of degradation with a degree of polymerization (DP) for paper less than 400. Therefore, a mass deacidification programme was introduced in the NUL in 2013. The key focus was on the selection of archival copies of the monographic print collection of “Slovenika,” with the date of publication from the middle of the nineteenth century onward. Based on the results of the PaperTreat project (Kolar et al. 2008; Balažic et al. 2007), Bookkeeper mass deacidification provided by the Preservation Technologies B.V. was used in the Netherlands (Preservation Technologies c) and afterward by the Hoogduin Preservation B.V. In addition to the efficiency of deacidification, an important factor to be considered is the side effects of the treatment. In the case of Bookkeeper treatment, very few side effects of the treatments, such as bleeding of stamps and inks, label damages, staining of the pages as a result of the dissolution of the binding materials and damage to bindings, were observed, with the exception of surface deposits, which were observed on almost all materials (Kolar et al. 2008).

The efficiency of a mass deacidification treatment and its sustainability are usually evaluated by two parameters: the pH of the paper after treatment and the alkaline reserve deposited in the paper structure. The beneficial effect of mass deacidification on cellulose stability was found to be strongly related to the amount of alkaline reserve deposited during mass deacidification treatments, independent of varying parameters of book papers (Ahn et al. 2013). Although some indication of alkali-induced β-elimination was found, it did not occur to the extent that significantly influenced the molar mass of cellulose (Ahn et al. 2012b).

However, when the efficiency of deacidification is evaluated, the distribution of alkaline compounds throughout the book paper matrix has been proven to be highly important (Ahn et al. 2012a). Previous studies have shown that even large amounts of alkaline agents are insufficient to significantly slow acid-induced degradation reactions after accelerated aging if they are located only on the paper surface (Ramin et al. 2009).

The recommendations of DIN (Hofmann and Wiesner 2011), ISO standard ISO/TS 18344:2016 (ISO 2016) and DIN 32701:2018-11 (DIN 2018) require the use of established analytical methods, such as pH (surface or extraction method) and alkaline reserve determination according to ISO (ISO 1994). As original books that are mass deacidified cannot be sampled, the standards ISO/TS 18344:2016 (ISO 2016) and DIN 32701:2018-11 (DIN 2018) prescribe the use of specified uniform test papers that are treated together with books in a deacidification process and then examined by using standardized test methods.

To test the efficiency of the deacidification process, accelerated thermal degradation has been accepted as the method of choice. The comparison of deacidified and nondeacidified samples during accelerated thermal degradation is based either on physical test methods or chemical analysis of cellulose parameters, such as the degree of polymerization (DP) (Potthast and Ahn 2017). The values after accelerated degradation are compared between deacidified and nondeacidified samples, and a relative increase in performance can be given as an efficiency factor.
indicating prolongation of paper lifetime compared to the untreated reference (Hubbe et al. 2017).

Due to the lack of recent studies on the Bookkeeper deacidification system and the need to evaluate the deacidification treatment on historical papers, the study presented in the following paper was carried out on two sets of nonvaluable historical books with acidic paper, which are kept in the NUL in several copies and were planned for withdrawal. The books were part of a commercial deacidification run supplied by the NUL.

The results of the analyses achieved before and after deacidification of the books using Bookkeeper treatment from the NUL are presented. The aim of the study was to evaluate the mass deacidification treatment on genuine acidic paper samples from books without historical value published from 1887 through 1974 that could be destructively analyzed.

Alkaline reserve content deposited on historical book papers after mass deacidification was measured and compared with two different test papers inserted by the treatment provider into the books to follow deposition of the alkaline reserve in the books, which cannot be tested destructively. To evaluate the paper lifetime extension, the paper pH values before and after deacidification treatment were measured as well as the degradation rate constants of untreated vs. deacidified paper samples after accelerated thermal degradation. SEM–EDS analysis was carried out to evaluate the distribution of MgO deposition on the paper surface and in the cross-section of the paper. To verify the results, the study was conducted on two sets of samples that were sent separately for the mass deacidification treatment.

**Experiment**

**Paper samples**

Two sets of nonvaluable historical books sent for Bookkeeper mass deacidification treatment together with the shipment of books from the NUL in 2018 (samples marked with a) and in 2019 (samples marked with b) to the Hoogduin Preservation B.V. in the Netherlands were investigated. The first set (a-1 to a-11) comprised randomly selected nonvaluable historical books published between 1890 and 1974, and the second set (samples marked with b-1 to b-13) was published between 1887 and 1969. Each set of books was deacidified in a different batch. Part of the bookblock was removed from the books to be used as reference historical papers (before deacidification). We have avoided selecting books with coated or supercalendered papers (Library of Congress).

Two test papers, Whatman filter paper No. 2 with at least 98% α-cellulose content and pH value 6.3±0.1 and Schut 100% cotton linters paper and pH value 6.1±0.1 (Schut Papier, Netherlands), were inserted by the Bookkeeper treatment providers into historical books to follow deposition of the alkaline reserve. Both papers are not surface sized. Untreated and deacidified historical paper samples a-1 to a-11 were subjected to accelerated degradation conditions at 80 °C and 65% RH for 6, 18, 14, 30 and 40 days in a Vötsch VC 0020 climatic chamber. Samples b-1 to b-13 were subjected to accelerated degradation conditions in the same chamber at 80 °C and 65% RH for 7, 14, 21 and 28 days. All paper samples were exposed to accelerated degradation as single sheets.

The samples for pH measurements after deacidification, accelerated degradation experiments and alkaline reserve determinations were taken from similar positions in the book.

**Analytical methods**

**pH measurements**

The pH of the water extracts was measured according to the standard TAPPI T 509 om-02 (TAPPI 2002), modified for smaller samples: 7 mL of deionised water was added to 100 mg of paper sample. The pH was determined in the water extract after one hour by using a flat membrane electrode (Metrohm 6.0256.100) connected to a Mettler Toledo MP 220 pH meter. The pH of the deacidified paper sample water extracts was measured after 48 h (Strlič et al. 2004).

**Determination of alkaline reserve**

Alkaline reserve was determined according to the ISO 10716:1994 standard (ISO 1994), adjusted for smaller samples (0.5 g of paper samples, in addition to 12 mL of distilled water and then 5 mL of 0.1 M HCl). The endpoint of titration was determined by using a methyl red indicator in the test paper samples.
case and by using a pH meter in the historical papers case (pH 5). Potentiometric titration was used as an alternative to the methyl red indicator procedure due to the yellow coloration of the historical sample solutions. All determinations were performed with duplicate measurements.

**Fiber furnish analyses**

Fiber furnish analyses were performed according to the ISO 9184 standard (ISO 1990) using a Nikon Eclipse 80 I digital microscope.

**Determination of weight average molecular mass**

The molecular mass of cellulose tricarbanilates (CTC) (Kolar et al. 2012; Stol et al. 2002) was determined by using size exclusion chromatography according to the procedure described by Malešič et al. (2021a).

To calculate the weight-average degree of polymerization (DPw) (Kolar et al. 2012), weight-average molar masses determined by SEC were divided by the molar mass of the carbanilated glucosidic monomer unit. Then, DPw was used to calculate the degradation rate constant of cellulose according to the Ekenstam equation (Ekenstam, 1936):

\[
\frac{1}{DP} = \left(\frac{1}{DP_0}\right) + k \cdot t
\]

where DP = degree of polymerization after accelerated degradation, DP0 = degree of polymerization before accelerated degradation, k = rate constant of degradation [h⁻¹] and t = time of accelerated degradation [h]. Higher values of k represent a higher rate of degradation of samples.

**Table 1** Acidic historical papers, publication years, fiber furnish analysis and pH values of paper samples before and after deacidification. The average standard deviation (SD) of the pH values was calculated from duplicate measurements

| Sample number | Year of publication | Fiber furnish analysis | pH values |
|---------------|---------------------|------------------------|----------|
|               |                     |                        | Before deac | SD | After deac | SD |
| a-1           | 1902                | 100                    | 5.40      | 0.05 | 7.2       | 0.2 |
| a-2           | 1924                | 91                     | 5.5       | 0.2  | 7.7       | 0.2 |
| a-3           | 1961                | 61                     | 6.7       | 0.1  | 8.4       | 0.01 |
| a-4           | 1890                | 58                     | 5.2       | 0.2  | 7.7       | 0.2 |
| a-5           | 1901                | 82                     | 5.3       | 0.2  | 6.8       | 0.2 |
| a-6           | 1976                | 100                    | 6.00      | 0.07 | 7.6       | 0.05 |
| a-7           | 1944                | 79                     | 5.70      | 0.06 | 7.7       | 0.1 |
| a-8           | 1931                | 61                     | 5.15      | 0.05 | 7.3       | 0.2 |
| a-9           | 1937                | 61                     | 5.4       | 0.1  | 7.4       | 0.2 |
| a-10          | 1956                | 63                     | 6.7       | 0.2  | 8.2       | 0.2 |
| a-11          | 1949                | 49                     | 6.9       | 0.1  | 8.6       | 0.1 |
| b-1           | 1969                | 77                     | 4.91      | 0.08 | 7.55      | 0.04 |
| b-2           | 1967                | 72                     | 5.7       | 0.1  | 8.4       | 0.3 |
| b-3           | 1951                | 63                     | 5.0       | 0.1  | 8.1       | 0.1 |
| b-4           | 1953                | 66                     | 4.9       | 0.1  | 7.4       | 0.1 |
| b-5           | 1939                | 62                     | 5.3       | 0.1  | 8.3       | 0.3 |
| b-6           | 1933                | 61                     | 4.84      | 0.09 | 7.7       | 0.1 |
| b-7           | Not known           | 55                     | 4.94      | 0.08 | 8.4       | 0.3 |
| b-8           | 1956                | 58                     | 5.44      | 0.06 | 8.2       | 0.1 |
| b-9           | 1925                | 52                     | 4.89      | 0.06 | 8.0       | 0.3 |
| b-10          | 1934                | 57                     | 4.4       | 0.1  | 7.1       | 0.1 |
| b-11          | 1927                | 70                     | 4.57      | 0.01 | 6.55      | 0.08 |
| b-12          | 1891                | 64                     | 4.60      | 0.07 | 6.3       | 0.2 |
| b-13          | 1887                | 33                     | 4.65      | 0.07 | 6.86      | 0.05 |
The standard deviation (SD) for determining the degradation rate constant ($k$) is calculated according to the Ekenstam equation using linear regression, where $k$ is the regression slope and SD is the error of the regression slope.

**SEM–EDS**

To evaluate the distribution of MgO deposition on the paper surface and in the cross-section of the paper, samples were characterized by using a FE-SEM Zeiss Ultra Plus microscope equipped with EDS (Oxford X-Max SDD 50 mm² detector, and INCA 4.14 X-ray microanalysis software). Sample preparation included cross-section polishing to obtain pristine cross sections of the selected papers (using a Jeol IB-19510CP Cross Section Polisher), fixation of the selected paper samples (surface and/or cross-section investigation) on conductive C-tape and subsequent sputtering with Au/Pd without any additional polishing. The EDS detector was calibrated just prior to the analysis with a Si standard under the operating conditions. The EDS spectra were recorded by using a process time of 5 s, lifetime of 120 s and 15 kV accelerating voltage, which is an acceptable compromise between the analyzed volume and the overvoltage needed for excitation to produce X-rays. Using the Anderson-Halser estimation (Friel and Lyman 2006), the X-ray production depth was calculated to be approximately 4.9 μm.

**Results and discussion**

The list of historical papers from the books studied in this research is presented in Table 1. The papers were taken from two sets of books with similar publishing periods (see description of the paper samples). After fiber furnish analysis (Table 1), different compositions of groundwood and bleached cellulose pulp were determined. Five paper samples also contain cotton fibers. The highest content of cotton fibers (46%) was found in the book with the earliest date of publication.

The results of the composition of the papers are consistent with the PaperTreat project survey (Kolar et al. 2008), which demonstrates that library monographs published between 1870 and 1990 were most often composed of ground wood pulp and bleached pulp in varying amounts or 100% bleached pulp. From 1850 to 1870, almost all papers were made from cotton fibers, and in the 1870s, groundwood pulp and bleached pulp began to replace cotton.

The pH values of the untreated paper samples ranged from $4.4 \pm 0.1$ to $6.9 \pm 0.1$, as was to be expected due to the use of acidic sizing agents from the mid-19th to the last decades of the twentieth century.

After mass deacidification, pH values were determined as described by Strlič et al. (2004) instead of following standard methods. For samples with alkaline aqueous extracts, the effect of atmospheric CO$_2$ and the slow dissolution of alkaline earth metal carbonates should be considered, which is not the case with any of the standardized methods for determination of the pH of paper. Since CO$_2$ represents a weak acid, it lowers the equilibrium pH of solutions of CaCO$_3$ and MgCO$_3$, the difference being more than 1.5 pH units (Strlič et al. 2004). The measured pH values after deacidification treatment were higher than those of untreated papers (Table 1), ranging from $6.3 \pm 0.2$ to $8.6 \pm 0.1$. The repeatability of the determinations, expressed as standard deviation, is comparable to the previous results, up to 0.3 pH units for alkaline samples (Strlič et al. 2004). Although a direct comparison of pH values is not possible, we estimate that the results are consistent with the range of possible pH results published by the treatment provider, which are between 7 and 10, with typical results in the range of 8.0–9.5 (Preservation Technologies b).

ISO/TS 18344:2016 and ISO 6588-1 standards describe only the pH value of the test paper measured in an aqueous extract (higher than 6.5 after deacidification) and not for the original papers, if investigated.

Alkaline reserve in test and historical papers

The second parameter for the evaluation of mass deacidification is the alkaline reserve content, where a large amount of sample paper is needed. To avoid destructive analysis of original books, the effectiveness of the mass deacidification process is usually examined by using a standardized test method on the test papers inserted in 10% of the treated books within one deacidification batch.

The test papers are treated together with the documents in a deacidification process. The standard ISO/TS 18344:2016 suggests acidic test papers (pH value approximately 5) with similar properties to common
paper quality produced in the period from approximately 1870 onward to ensure reliable results.

The Bookkeeper treatment providers used two papers (Whatman filter paper No. 2 and Schut paper) that do not correspond to the ISO/TS 18344:2016 standard. Preservation Technologies B.V. in the Netherlands (Preservation Technologies c) used Schut paper. Both papers have higher pH values, are not sized and do not contain a kaolin filler, as suggested in the ISO/TS 18344:2016 standard.

To verify the suitability of the Whatman and Schut test papers, both papers were inserted into the books studied during mass deacidification; the alkaline reserve for two test and historical book papers was measured and compared.

Alkaline reserves were measured in the central area of paper. Historical papers from books b-1 to b-13 (Table 1) were sampled next to the inserted test papers to ensure a similar position in the bookblock.
The papers with pH values below 5 before deacidification (b-1, b-3, b-4, b-6, b-7, b-10, b-11, b-12, b-13) had a significantly lower alkaline reserve content after deacidification (below 1 wt% CaCO₃) (Figs. 1, 2). The content is also significantly lower than the content in Whatman test paper. The samples with pH values higher than 5 (b-2, b-5, b-8) have an alkaline reserve above 1 wt% CaCO₃, which is comparable to the Whatman test paper alkaline reserves (Figs. 1, 2).

Therefore, the conclusion is that the Whatman test paper can only be used as a reference paper for papers with pH values above pH 5. For papers with pH values below 5, we have to consider that more alkaline substance is used in the process of neutralization; therefore, only the surplus of alkali can serve as an alkaline reserve; consequently, the alkaline reserve content in the Whatman test paper is higher.

For Schut paper, the alkaline reserve contents are significantly higher in comparison to either historical papers or to Whatman test paper. The values are not comparable even in the same pH range. The reason for such differences can be the different surface characteristics of the paper, which are rougher in comparison to Whatman test paper and might lead to a better adsorption of MgO by the paper.

The alkaline reserve content in the test papers is in accordance with the requirements of the NUL (higher than 1.0 ± 0.2 wt% of CaCO₃ in the paper), which were set according to the Library of Congress (Library of Congress) guidelines. More than half of the examined historical papers contain a lower alkaline reserve content (below 0.8, Table 2); however, ten out of thirteen samples reached 0.5 wt% expressed as MgCO₃ or 0.59 wt% CaCO₃ in the paper, which is the requirement of the ISO/TS 18344.2016(E) (ISO 2016).

According to the results (Tables 1 and 2) and Figs. 1 and 2, the conclusion is that the alkaline reserve content in the papers with similar compositions and comparable pH values can be completely different after the mass deacidification process. The results also strongly depend on the properties of a paper, such as porosity, thickness, sizing, and coating. (ISO 2016). Therefore, one standard type of paper, available in the market, should be used. Both test papers used by the Bookkeeper providers are not surface sized and have a completely different composition in comparison to the historical papers studied (Table 1) and do not provide comparable results with historical papers. However, if Whatman No. 2 filter paper is used as a test paper, the requirements for the alkaline reserve content in the test papers must be adjusted to be at least 0.5 wt% higher to achieve the desired values in the historical papers after mass deacidification. According to the obtained results and to assure the effectiveness of paper deacidification, the recommendation is to add books with acidic paper to the batch with similar properties as historical papers from the nineteenth century onward as required by the ISO standard (ISO 2016).

Homogeneity of alkaline reserve in the deacidified books

The homogeneity of the alkaline reserve, set by the ISO standard (ISO 2016), describes only the distribution of alkaline substances over the entire surface area of the bookblock and not its distribution in the cross-section of the bookblock. In the standard, each A5 test paper is cut into 6 different segments, and 3 pieces are put together to measure the alkaline reserve. In this study, the homogeneity of the alkaline reserve distribution in the cross-section of the book was examined. Therefore, due to the high amount of sample material needed to test the alkaline reserve (ISO 1994), the alkaline reserve content was measured in the central area of each historical paper from

| Sample | Alkaline reserve (wt% CaCO₃) | SD  |
|--------|-----------------------------|-----|
| b-1    | 0.67                        | 0.03|
| b-2    | 1.16                        | 0.07|
| b-3    | 0.8                         | 0.1 |
| b-4    | 0.48                        | 0.07|
| b-5    | 1.2                         | 0.1 |
| b-6    | 0.66                        | 0.01|
| b-7    | 0.80                        | 0.07|
| b-8    | 1.2                         | 0.1 |
| b-9    | 0.76                        | 0.01|
| b-10   | 0.31                        | 0.04|
| b-11   | 0.40                        | 0.02|
| b-12   | 0.66                        | 0.04|
| b-13   | 0.48                        | 0.06|
the book in duplicate. The alkaline reserve of papers in the books was determined at the beginning (front), in the middle or at the end of the textbook. If the book had few pages, only the alkaline reserve of papers at the beginning and at the end of the bookblock were measured.

Additionally, alkaline reserve content was measured in the Schut test papers, which have been added to the text block. The results (data not shown) confirm the results presented in Fig. 1 that the alkaline reserve was above 1.0 ± 0.2 wt% CaCO₃ in all of the test papers, and there was no correlation between the determined alkaline reserve in the historical book papers and in the test papers. The Library of Congress requirement determines the homogeneity of alkaline reserve for a given paper type to vary from specified optimal concentrations no more than 20% between books and within individual pages (Preservation directorate, 2004).

As evident from Fig. 3 and Table 3, only two books out of eleven reached the value of 1.0 ± 0.2 wt% CaCO₃ in the paper as requested by the NUL, and three books reached 0.59 wt% CaCO₃ in the paper required by the ISO/TS 18344.2016(E). The homogeneity of mass deacidification was below 20% on 5 samples out of 11, which is less than half of the samples (45%). Some of the books exhibit very low homogeneity of alkaline reserves, with values exceeding 100% over the bookblock.

On average, the results of alkaline reserve in historical papers are (Tables 2 and 3) significantly lower in comparison to the Preservation Technologies assertions that the treatments results in the typical reserve of 1.5 wt% CaCO₃ in the paper (Preservation Technologies b). If all examined samples (Tables 2 and 3) are considered, only 33% of the samples reached the value 1.0 ± 0.2 wt% CaCO₃, and 62% of the samples reached 0.59 wt% CaCO₃ in the paper as required by the ISO/TS 18344.2016(E).

Comparison between the pH values and the alkaline reserve contents in historical papers

Due to its protective role, the amount of alkaline reserve should be one of the decisive parameters in the optimization or evaluation of deacidification treatments, along with the achieved pH value (Strlič and Kolar, 2005). There is no correlation between the alkaline reserve content and the pH values of the samples (a-1 to a-11 and b-1 to b-13) after deacidification. The pH values can only be used to predict the presence of an alkali reserve but not to determine its
content, as already shown by Saverwyns et al. (2002). Additionally, studies on the dependence of the pH of different papers, including Whatman filter paper and acidic papers, on the amount of alkaline reserve demonstrate different behavior of the papers due to a buffer effect in the rosin-sized paper samples (Strlič and Kolar, 2005). Therefore, the pH measurements of the test papers could not be used to estimate the pH values of historical paper samples.

Distribution of Mg-rich particles on the surface and in the cross-section of paper samples

To evaluate the distribution of Mg-rich particle (Polovka et al. 2006) deposition on the paper surface and in the cross-section of the paper, SEM EDS analyses of the paper samples were performed. The results of the analyses were comparable for the different samples; therefore, only the results of the b-3 sample are presented as representative. Lightly colored points in element maps represent a higher content of the listed elements.

The results of the SEM–EDS analysis carried out on the untreated paper surface of sample b-3 (Fig. 4) indicate the presence of Al, Si, S and Fe. Al and Si are due to the use of clay in paper production, which could be expected, as printing papers made before the end of the twentieth century contained clay fillers (Hubbe and Gill 2016). Al and S are present because of the use of aluminum sulfate as a sizing
agent. Sulfur is very homogeneously distributed on the paper surface but in a lower amount compared to Al or Si.

A small amount of iron was also detected (not presented in Fig. 4), which is not surprising, since the transition of metal ions is generally present in machine-made paper from processing machinery and the water used in its manufacture (Williams et al. 1978).

After deacidification treatment, Mg-rich particles could be detected (Fig. 5), but they were not uniformly distributed across the paper surface. The sizes of the Mg-rich particles vary from ~400 nm to ~3.7 μm with an average size of approximately 1 μm, which is consistent with the data from the Bookkeeper providers (Preservation Technologies b).

Previous studies showed that Al(III) ions, present in the paper due to alum-rosin sizing, responsible for increased acidity in the papers, are homogeneously dispersed throughout the paper mass, which is a consequence of the internal sizing of the paper (Jablonský and Šima 2020). Therefore, for the efficiency of deacidification, the distribution of alkaline compounds throughout the book paper matrix has been proven to be highly important (Buchanan et al. 1994; Ahn et al. 2012a). According to the literature (Potthast and Ahn 2017), the size of the dispersed particles is an essential factor to penetrate the whole cross-section of a paper sheet. Furthermore, to protect the cellulose on a quasi-molecular level within the cellulose fibrils, the critical issue is not just penetration of deacidification compound (MgO) into the larger-pore paper web but rather its penetration into the cellulosic fibers themselves (Potthast and Ahn 2017). The average pore size in the

![Fig. 6 Magnesium distribution maps throughout the cross-section of the b-3 paper sample; a untreated, b after the deacidification treatment – treated, and c artificial thermal degradation—treated, aged](image-url)
macroscopic paper web is roughly between 1 and several μm (Resch et al. 2010; Bennis et al. 2010), while the average pore size in pulp fibers is approximately 1–100 nm (Andreasson et al. 2003; Aarne et al. 2012; Lovikka et al. 2016). The MgO particles used in the researched deacidification process may be small enough to penetrate the paper matrix (at least in larger pores); however, they seem to be too large to invade individual pulp fibers. Therefore, to examine this assertion, the Mg-rich particle distribution was analyzed by using SEM–EDS in the paper cross-section. After deacidification treatment (Fig. 6b, treated), Mg-rich particles were detected only on the surface of the paper sample, and even accelerated degradation conditions (Fig. 6c) did not influence the distribution of the particles in the paper cross-section within the pulp fibers. The results agree with Ramin et al. (2009), in which a comparative study of different deacidification treatments was performed. The measurements of magnesium content through the paper done by XRF showed that the Mg-rich particles remain primarily on the paper surface, while only a few Mg-containing particles have diffused into the paper core. In contrast, using other tested deacidification methods, such as immersion of paper samples in aqueous

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**Fig. 7** 1/DP–1/DP₀ as a function of accelerated degradation time for paper sample b-3 with pH value 5.0 ± 0.1 and b-3 BK after deacidification treatment with a pH value 8.1 ± 0.2 and containing 0.8 ± 0.1% alkaline reserve, expressed in wt% CaCO₃

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**Fig. 8** Degradation rate constants of untreated and deacidified (BK) paper samples vs. pH value of the samples. The outlier on the top left is paper sample b-13
magnesium and calcium hydrogen carbonate solution and the Booksaver method, based on immersion in a nonpolar magnesium solution, revealed that magnesium ions could spread through the paper cross-section, thus depositing the Mg-containing phase after drying well within individual pulp fibers (Ramin et al. 2009).

Degradation of paper

The degradation rate constants of the paper samples during accelerated thermal degradation at 80 °C and 65% RH were calculated from DPw according to the Ekenstam equation. The equation well describes the data of paper during degradation due to acid hydrolysis (Strlič and Kolar 2005), and although others propose a modified equation to better describe the degradation kinetics (Jablonsky et al. 2018), the Ekenstam equation was used. The data for either untreated or deacidified paper samples were correlated (Fig. 7), and an intercept close to zero for a plot \[\frac{1}{DP1/DP0}=f(t)\] and a regression coefficient \((R^2)\) close to 1 were observed.

The untreated sample degradation rates slow down with increasing pH value of the paper samples (Fig. 8). The only exception was paper sample b-13 (pH=4.6, \(k=42 \mu\text{mol-mol}^{-1}\text{-day}^{-1}\)), which had a significantly higher degradation rate constant, which might be due to the presence of both iron and copper, as proven by SEM–EDS analysis (data not shown). The same would be expected if the degradation rate constants of all paper samples (together with the deacidified ones) were compared with their pH values. In contrast, although the degradation rate of paper depends crucially on the pH of the paper, no correlation could be found between the degradation rate constant of all untreated and deacidified papers and the corresponding pH values (Fig. 8).

After the treatment of books and papers with a nonaqueous dispersion of alkaline particles such as MgO, which does not necessarily result in the desired neutralization of acidic species within the fibers affecting the paper due to incomplete deacidification, the acids may still remain in the fibers and core of the paper (Hubbe et al. 2017). In this case, the conventional pH determination, which gives us an average pH of the paper extract and even allows competition of the reaction due to wetting, can neither be used to evaluate deacidification treatment nor to estimate paper stability, as shown in Fig. 8.

The efficiency factor (EF) estimates the prolongation of paper lifetime after a deacidification treatment

**Fig. 9** Calculated efficiency factors for paper samples a-1 to a-11 and b-1 to b-13 during accelerated thermal degradation at 80 °C and 65% RH.
relative to a nontreated sample. It was calculated from degradation rate constants during accelerated thermal degradation of untreated \((k)\) or deacidified paper samples \((k_{BK})\):

\[ EF = \frac{k}{k_{BK}}. \]

Our previous evaluation of the Bookkeeper treatment (Malešič et al. 2021a, b) on two different model acidic papers with \(2.4 \pm 0.1\) and \(2.5 \pm 0.1\%\) alkaline reserves, expressed in wt\% CaCO\(_3\), showed that the treatment decreased the degradation rate constants of the papers. The efficiency factor was different depending on the paper sample, with values of \(1.5 \pm 0.2\) and \(2.1 \pm 0.4\) (Malešič et al. 2021a, b). The results of the PaperTreat project, carried out on one paper sample, show that at 20 °C, deacidified paper using Bokkeeper dispersion is 3.3 times more stable than the untreated paper with pH 6.2 (Balažic et al. 2007).

In contrast, despite the higher pH value and alkaline reserve obtained after deacidification of historical papers, the degradation rate constants measured after deacidification treatment are in most cases similar to the untreated ones, yielding efficiency factors of approximately 1 (Fig. 9). Only paper sample a-11 was excluded from the measurements due to its pH value in the neutral region before deacidification (pH \(6.9 \pm 0.1\)). Considering the standard deviation, the highest stabilization factors up to 1.7 were achieved only in the case of two paper samples out of 23, and only 4 paper samples out of 23 exhibited the stabilization effect of the treatment with an efficiency factor above 1. When the results of measurements were calculated as the number of chain scissions (NCS), according to Potthast and Ahn (2017), before and after accelerated degradation, we obtained the same results considering the error of the measurements.

No correlation was found between the alkaline reserve obtained after deacidification and the stability factors or the degradation rate constants measured after deacidification treatment are in most cases similar to the untreated ones, yielding efficiency factors of approximately 1 (Fig. 9). Only paper sample a-11 was excluded from the measurements due to its pH value in the neutral region before deacidification (pH \(6.9 \pm 0.1\)). Considering the standard deviation, the highest stabilization factors up to 1.7 were achieved only in the case of two paper samples out of 23, and only 4 paper samples out of 23 exhibited the stabilization effect of the treatment with an efficiency factor above 1. When the results of measurements were calculated as the number of chain scissions (NCS), according to Potthast and Ahn (2017), before and after accelerated degradation, we obtained the same results considering the error of the measurements.

The dispersion methods of deacidification are generally much less effective in comparison to deacidification in homogeneous solutions (Hubbe et al. 2017; Katuscak et al. 2012; Ramin et al. 2009) due to a better penetration of both the macroscopic paper matrix with its large pores and voids, which some dispersion methods are able to reach (Potthast and Ahn 2017), and the cellulose fibers with its much smaller pores, which homogenous reagent solutions can enter; however, dispersed particles fail to access due to their sheer size. The results of the SEM–EDS analysis, the research by Ramin et al. (2009) and our previous study (Malešič et al. 2021a, b), show that most of the Mg-rich particles are unable to penetrate the paper matrix even after Bookkeeper deacidification treatment. Thus, they remain on the paper surface and therefore cannot neutralize the acids present in the paper, which results in low long-term efficiency of the deacidification treatment.
The reasons for the discrepancies in the Bookkeeper treatment efficiency between different studies (Buchanan et al. 1994; Balažič et al. 2007; Ramin et al. 2009; Katuscak et al. 2012; Malešič et al. 2021a, b) are most likely due to the very different properties of the model papers compared to historical papers. We have shown in the previous chapter that the alkaline reserve contents in the papers with similar compositions and comparable pH values can be completely different after the mass deacidification process because the results of the treatment also depend on the properties of a paper, such as porosity, thickness, sizing, coating, etc. In the previous studies (Buchanan et al. 1994; Balažič et al. 2007; Ramin et al. 2009; Katuscak et al. 2012; Malešič et al. 2021a, b), a limited number of model paper samples, usually blank sheets of different paper types, were used. Therefore, we can also assume that in the case of printed historical papers, the penetration of Mg-rich particles into the paper matrix is even more limited, resulting in lower efficiency factors of the treatment.

Conclusions

The Bookkeeper mass deacidification process was systematically evaluated on two sample sets of 24 historical books with acidic paper from the late nineteenth century to the 1980s by using standard analytical methods, such as pH and alkaline reserve determination. After the deacidification treatment, the measured pH values were higher in comparison to untreated papers, ranging from 6.3 ± 0.2 to 8.6 ± 0.1. The measurements of the alkaline reserve in the papers showed that 62% of the samples reached a value of 0.59, expressed as wt% CaCO₃ in the paper, as required by the standard ISO/TS 18344:2016. However, when the alkaline reserve content was compared at the beginning, in the middle and at the end of the same bookblock, the measurements differed by less than 20% in only 45% of the samples. Some of the books studied showed a very large inhomogeneity of alkaline reserve across the bookblock. The use of two different types of test papers (Whatman and Schut) to determine the alkaline reserve content in historical papers was investigated. When alkaline reserves are estimated from test papers, it should be considered that variations between papers are possible even in the same pH range, as different paper types build up different alkaline reserve contents.

The distribution of Mg-rich particles used in the Bookkeeper deacidification process on the paper surface and in the cross-section of historical papers was monitored using SEM–EDS. Mg-rich particles of different sizes are unevenly distributed over the surface of the paper. Furthermore, the cross-section analysis showed that after the deacidification treatment, Mg-rich particles were only detected on the surface of the paper sample, and the accelerated degradation conditions had no influence on the distribution of Mg-rich particles in the paper cross-section within the pulp fibers. The efficiency factors determined after accelerated thermal degradation of untreated and treated paper showed that the deacidification treatment with Bookkeeper has only very limited effectiveness for the majority of the paper samples tested. The results indicate that even though pH values and alkaline reserves reach the recommended values after the deacidification treatment, the treatment does not have a significant effect on the stability of the paper unless the alkaline particles are homogeneously distributed and can neutralize the acidity in the paper fibers or the core of the paper. Therefore, in the case of deacidification by nonaqueous dispersions of alkaline particles such as MgO, the established methods for determining pH and alkaline reserve cannot be used to evaluate treatment stability.

The comparison of these results with previously published results based on model paper samples to evaluate the Bookkeeper treatment efficiency confirms the need for the greatest possible authenticity of the samples.

Acknowledgments The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P1-0153, No. P1-0175 and basic research project No. J4-1764). Ana Šiško and Eva Korenčič are gratefully acknowledged for technical assistance. We gratefully thank Janja Korošec for language editing.

Author Contributions All authors contributed to the study conception and experimental design. Material preparation, data collection and analysis were performed by Jasna Malešič and Marjan Marinšek. The first draft of the manuscript was written by Jasna Malešič, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.
Funding  This work was financially supported by Slovenian Research Agency (research core funding No. P1-0153, No. P1-0175 and basic research project No. J4-1764).

Declarations

Conflict of Interests  The authors have no relevant financial or nonfinancial interests to disclose.

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