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Accelerated Aging of Deacidified and Untreated Book Paper in 1967 Compared with 52 Years of Natural Aging

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Abstract: Three copies of a book that had been optionally deacidified using two different procedures in 1967, and then subjected to accelerated aging, were tested again after 52 years of natural aging. Matched copies of the book *Cooking the Greek Way*, which had been printed in Czechoslovakia on acidic paper, were evaluated. Nonaqueous treatment of two of the copies with magnesium methoxide dissolved in chlorofluorocarbon solvent had been found in 1967 to have decreased the susceptibility to embrittlement, as evidenced by the results of the accelerated aging, followed by folding endurance tests. Retesting of the same books in 2019, after 52 years of room temperature storage, showed that the deacidification treatments had achieved the following benefits in comparison to the untreated book: (a) higher brightness; (b) higher folding endurance; (c) tensile breaking length higher in the cross-direction of the paper; (d) substantial alkaline reserve content, (e) an alkaline surface pH in the range 7.1–7.4, and (f) higher molecular mass of the cellulose. Remarkably, some of the folding endurance results matched those of unaged samples evaluated in 1967. Scanning electron micrographs showed no differences between the treated and untreated books.

Keywords: cellulose, mass deacidification, magnesium alkoxide, paper properties

Richard D. Smith, in memoriam, formerly owner of the Wei T'o Company based on his inventions related to mass deacidification.

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Langfristige Wirkung von Entsäuerungsmaßnahmen: ein Vergleich von künstlich gealtertem und 52 Jahre natürlich gealtertem Papier

Zusammenfassung: Zwei Exemplare eines auf säurehaltigem Papier gedruckten Buches wurden 1967 optional mit zwei verschiedenen Verfahren mit Magnesiummethoxid gelöst in Fluorchlorkohlenwasserstoff entsäuert; ein drittes Exemplar wurde als unbehandelte Referenz aufbewahrt. Alle Exemplare wurden danach künstlich gealtert. Anschließende Falztests bestätigten, dass diese Behandlung die Stabilität des Papiers erhöhte. Nach 52 Jahren natürlicher Alterung bei Raumtemperatur wurde das Papier dieser Bücher 2019 erneut getestet. Die Entsäuerungsbehandlungen hatten im Vergleich zum unbehandelten Buch folgende Auswirkung auf das Papier: (a) höhere Helligkeit; (b) erhöhte Falzzahl; (c) erhöhte Zugfestigkeit quer zur Faserrichtung; (d) erhöhter Gehalt an alkalischer Reserve, (e) pH-Wert im Bereich von 7,1 bis 7,4 und (f) höhere Molmasse der Cellulose. Bemerkenswerterweise stimmten einige Ergebnisse der Falztests mit jenen der 1967 ausgewerteten nicht gealterten Proben überein. Rasterelektronenmikroskopische Aufnahmen zeigten keine Unterschiede zwischen den Papieren behandelter und unbehandelter Bücher.

Le vieillissement accéléré du papier de livres désacidifié et non traité en 1967 en comparaison à 52 ans de vieillissement naturel

Résumé: Trois copies d´un livre, dont deux désacidifiés avec deux méthodes différentes en 1967 et ensuite soumis à vieillissement accéléré ont été testés de nouveau après 52 ans de vieillissement naturel. Des exemplaires assortis du livre “Cuisiner à la grecque” imprimés en République Tchèque sur papier acide ont été évalués. Un traitement non aqueux de deux exemplaires avec du méthoxyde de magnésium dissous dans un solvant de chlorofluorocarbone ont en 1967 diminué la tendance à l´émiettement et cela a été confirmé par les résultats de vieillissement accéléré suivis de tests de résistance à la pliure. Les nouveaux tests conduits en 2019 sur les même livres après 52 ans de stockage à température ambiante montrent que les traitements de désacidification ont eu en outre, en comparaison avec le livre non traité ces bénéfices complémentaires: (a) une blancheur plus élevée

(b) une résistance à la pliure plus élevée (c) une longueur de rupture sous tension en coupe transversale du papier plus élevée (d) une réserve alkaline importante (e) un pH alcalin de surface entre 7,1 et 7,4 et (f) une masse moléculaire de la cellulose plus élevée. Il est intéressant de noter que certains des résultats des tests de résistance à la pliure recoupent ceux des échantillons non vieillis évalués en 1967. Les images SEM n´ont pas montré de différence entre les livres traités et celui non traité.

1 Introduction

The authors had the rare opportunity to re-test a unique set of three books, two of which had been deacidified in 1967, and which also had been subjected to accelerated aging and physical testing in 1967 (Smith 1970, 1972). Given this opportunity, a main goal of this work was to examine the effects of 52 years of natural aging on the paper properties and to compare those differences with the predictions based on the accelerated aging test carried out in 1967. A further goal was to assess the performance of the deacidification treatments performed in 1967.

Forty years ago, an article titled "Comparison of accelerated aging of book paper in 1937 with 37 years natural aging" was published in this journal (Wilson and Parks 1980). Those authors noted that "planning and executing an experiment over a period of 20–50 years is very difficult". Test procedures often change with time, and essential samples may become lost or discarded. The cited authors overcame such challenges and ultimately were able to provide some of the most persuasive evidence to date supporting the use of accelerated aging tests to predict aspects of natural aging of paper. In particular, it was found that accelerated aging tests, carried out on a diverse set of paper specimens, were able to predict a rank order of the paper's susceptibility to loss of folding endurance and other strength attributes.

An additional aspect to be considered in the present work is a mass deacidification treatment. In his Ph.D. research leading to the development of the Wei T'o system of mass deacidification, Richard D. Smith treated two matched sets of books with solutions of magnesium methoxide in a chlorodifluormethane (Freon-22) or dichlorodifluormethane (Freon-12) solvent under two sets of conditions (Smith 1970). A third set of the books was untreated. After drying and equilibration of the books with air, pages were subjected to accelerated aging (TAPPI Method T 534). As will be discussed in the present article, the results of accelerated aging tests supported a prediction of much slower aging of the specimens that had been deacidified. In particular, the folding endurance values of the deacidified paper did not decline nearly as much as the untreated paper when exposed to the accelerated aging conditions. According to Smith (1972), "When the solution

contacts the cellulosic material to be treated, the deacidification agent will react with and neutralize acidic compounds and functional groups such as sulfuric acid and carboxylic acid groups."

From approximately the early 1800s up to about 1990, it was common for the paper used in the printing of books to be prepared under acidic papermaking conditions (Hubbe 2005). It also has been well established that paper having an acidic extract pH undergoes progressive loss of strength during ordinary storage (Baty et al. 2010; Wilson and Parks 1979). Books manufactured more recently, throughout the world, generally have much better storage stability due to the widespread use of calcium carbonate, an alkaline mineral, as a filler for paper.

The deacidification system employed by Smith has been described in detail in a recent review article (Hubbe et al. 2018). Briefly stated, the original formulation pioneered by Smith involved magnesium methoxide dissolved in a chlorodifluoromethane solvent. The concept is that the agent can react with acidic compounds present in the paper according to Eq. (1), where "R" corresponds to the methoxide group in the cases to be considered. The "R′" symbol refers to various other groups or polymers that might be present in the acidic paper associated with carboxylic acids.

$$Mg(OR)_2 + R'COOH \rightarrow ROMg - OOCR' + ROH \quad (1)$$

In addition, the reagent also combines with the minor water content present in the dry paper (e.g. about 1–6%, depending on the relative humidity and other factors), according to the following equation:

$$Mg(OR)_2 + H_2O \rightarrow MgO + 2\,ROH \quad (2)$$

The MgO is understood to be susceptible to subsequent reaction with CO_2 and H_2O in the air or within the paper, according to:

$$MgO + CO_2 \rightarrow MgCO_3 \quad (3)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (4)$$

Equations (3) and (4) yield compounds that can serve as alkaline reserve materials in the paper (Hubbe et al. 2017). Various tests have shown the effectiveness of deacidification treatments involving nonaqueous solutions that were similarly effective as those outlined above (Ahn et al. 2012; Hubbe et al. 2017). Notably, however, none of the cited studies included natural aging.

Though the work of Wilson and Parks (1980) gave evidence of the validity and usefulness of the accelerated aging tests employed in the present work, there has been a lack of consensus regarding the most suitable conditions to be used in accelerated aging tests. The concentration of water molecules (humidity) in the air used for accelerated aging has been shown to have a major accelerating effect on

strength loss (Zervos 2010). It is well known that if a selected sample of ambient air is heated, its relative humidity will be decreased (Hubbe et al. 2017). It follows logically that to keep the relative humidity constant, a higher proportion of water molecules to air will be needed at the elevated temperature selected for the accelerated aging. As shown in Table 1, various humidity levels have been employed by researchers and listed in standards for accelerated aging of paper. An argument in favor of using hot humid conditions is that it favors hydrolysis reactions (Arney and Chapdelaine 1981; Zou, Uesaka, and Gurnagul 1996a, 1996b), which are believed to play a dominant role in the natural aging of typical paper samples. A possible concern is that excessively humid conditions might be too aggressive to be able to predict the relative effects of natural aging on different paper specimens.

2 Materials & Methods

2.1 Original Manuscript Samples

In 1967 Richard D. Smith purchased matching copies of the book *Cooking the Greek Way* (author: Maro Duncan, publisher: Spring Books, London, ISBN-13: 978-1112710018) at a local bookstore in Chicago. This 1964 copyrighted book was printed in Czechoslovakia. As stated by Smith (1972), the paper in the books comprised about 50% softwood groundwood pulp and 50% softwood sulfite pulp.

2.2 Treatments

In addition to the untreated books (default), two conditions of deacidification treatment were applied in 1967. Treatment was carried out with the hard-covered books in their "closed" format, except that a cotton wrapping cord was placed between the fly and the text leaves close to the spine. The books to be treated were

Table 1: Temperature and Relative Humidity Levels Specified in Various Standard Accelerated Aging Protocols.

Temperature (°C)	Relative humidity (%)	Standards, key references
100	>0.5% (sealed tube)	ASTM D 6819-02 (ASTM D 2002); ISO 5630-5
105	*ca.* 1.4% (dry oven)	TAPPI T453, ISO 5630-1; Rasch 1931
90	25	ISO 5630-2, TAPPI T544 (both superseded versions)
90	50	TAPPI T544 sp-03
80	65	ISO 5630-3

individually placed in an autoclave constructed from an eight-inch diameter galvanized steel water pipe with case iron flanges. The orientation of the books was top-down, such that the upper half of each book was fully immersed during the treatment. Quarter-inch glass tubing was placed at the base of the vessel to facilitate emptying of fluid below the level of each book at the end of treatment.

For "hot" treatment, each book was placed in the autoclave, which was bolted shut, and the assembly was placed in boiling water. The book was dried for 4 h, with the application of vacuum (667 Pa). The autoclave was then sealed, removed from the boiling water, and allowed to cool overnight. Nonqueous deacidification solution was prepared by first adding 500 ml of a 7% solution of magnesium methoxide in methanol into a 4.54 kg (10 lb) propane bottle. The solution was then diluted with 4.54 kg of chlorodifluoromethane (Freon 22). The deacidification solution was induced to flow into the autoclave by cooling the latter with dry ice. The amount of liquid was sufficient to immerse the upper half of each inverted book. The autoclave was then placed in hot water to finish the drying process of the book and to ensure impregnation throughout the material. The pressure in the autoclave rose to 2070 kPa (300 psi). The water temperature was lowered to 37.8°C (100°F) to give an autoclave pressure of 1379 kPa (200 psi). After 1 hour of immersion, the autoclave was removed from the water bath. The deacidification solution was blown out through a lower outlet. After 10–15 min, the autoclave was opened, and the book was judged to be substantially dry.

For the "cold" treatment, there was no heating and drying step. Instead, the autoclave, with the books inside, was packed in dry ice, such that any freezable water was frozen. The deacidification solution was prepared by using 5.44 kg (12 lb) of dichlorodifluoromethane (Freon 12) in place of the chlorodifluoromethane. The remaining treatment conditions were essentially the same as for the "hot" treatment.

Accelerated aging tests were carried out in 1967 with paper specimens taken from the top half of each of the three copies of the book *Cooking the Greek Way*. Such a position corresponded to the part of the book that would have been fully immersed in deacidification solution in the case of the treated books. The dry-oven conditions employed were similar to those of TAPPI Method T534 and ISO 5630-1, except that the temperature was 100°C rather than 105°C. The time of accelerated aging was from zero to 18 days.

2.3 Paper Property Tests Carried Out in 1967

The tests that were conducted in 1967 were recorded in the thesis document (University of Chicago) of Richard M. Smith, and also in US Patent 36,76,055 (Smith 1972). The procedures are briefly described as follows:

Specimens were taken from pages 71 to 90 and subjected to aging periods of 0, 3, 6, 9, 12, 15, and 18 days according to the TAPPI T 453 ts-63 procedure (Relative stability of paper, by effect of heat on folding endurance). MIT fold tests were carried out based on TAPPI Method T 511 with a 0.5 kg mass. Specimens that had been fully immersed in the deacidification solution were compared with specimens from the untreated book. Surface pH was evaluated according to TAPPI Method T 529, using a flat-ended combination pH probe and distilled water.

2.4 Tests Carried Out in 2019

The three books that were evaluated in 2019 were the same identical books as described in the thesis work (Smith 1970) and not the duplicate set described in the corresponding patent (Smith 1972). Each book had been separately stored within a padded brown paper envelope. The three envelopes containing the books were kept within a corrugated paperboard box, which had been sealed with paper tape. The box had been kept under typical room conditions during the period from 1967 to 2019.

2.4.1 Brightness and Color

The tests related to brightness and color were performed on patches of paper large enough to avoid the visual effects of any of the ink on either side of the page. These patches were generally at least 25.4 mm in diameter, found on pages 63, 87, 99, 119, 129, 133, 137, 143, and 161 of *Cooking the Greek Way*. The backing of each of these was 10 sheets of copy paper with 90% brightness. The book sample and sheets of copy paper were placed under the spectrophotometer (ColorTouch X, Technidyne Corp.). Each sample was averaged over 10 readings, which were automatic and 10 seconds apart. The pages were held flush against the lens to remove any angle or shadow, which uneven placement may incur. Measurements were taken from both the front and the back of each patch. Ten pages per book were tested, both in a central region and along the edge of the page. This distinction was made because of possible changes in composition from the atmosphere and/or uneven distribution of the treatment through the book.

2.4.2 MIT Folding Endurance Testing (TAPPI Method T 511 om-96)

Strips were cut to be 15 mm wide, generally achieving a length of around 200 mm in the machine direction and around 120 mm in the cross direction. These were then tested for standard MIT fold endurance, using clamps to affix the paper. The MIT

Folding Endurance Tester was from Tinium Olsen, Testing Machine Co., Willow Grove, PA. The strips were held in tension during the folding motions with a 0.5 kg equivalent weight applied with a spring. TAPPI standards use a 1 kg weight, but this was adapted to imitate the tests done by Richard Smith at the time of the treatment application. The number of folds was counted automatically. 40 strips from each book were tested, 20 in the machine direction and 20 in the cross direction.

2.4.3 Tensile Strength Testing (TAPPI Method T 494 om-96)

Tensile strength testing was done using a Horizontal Tensile Tester, model 84-56-00-003 from Testing Machines Inc (TMI). Strips were cut one inch wide, according to TAPPI standards, spanning the length of the page, around 25 mm. The basis weight of the paper averaged 75.65 g/m^2 and the caliper 0.123 mm, which were input in settings of the tensile testing and reflected in the results. The strips were inserted until flush against the back of the machine, and the following data were recorded: force (N), strength (kN/m), stretch (%), TEA (J/m^2), stiffness (kN/m), E-mod (GPa), and breaking length (km). 40 samples were taken from each book, twenty machine-directional and twenty cross-directional. These were taken from approximately the center of where the treatment was dispersed on the page.

2.4.4 Alkaline Reserve Testing (TAPPI Method T 553 pm-92)

First, the moisture content of the samples was determined with a revision of T 550 om-08. The samples were weighed, dried at 100°C for 30 min, and then kept in a sealed container until they cooled to room temperature. Five samples were taken from each book, then averaged to determine oven dry (OD) weight of the paper, which was then used for calculation of alkaline reserve.

One molar solutions of hydrochloric acid and sodium hydroxide were diluted to achieve the 0.1 N solutions required by the TAPPI standard. Based on average weights, 1 g OD is 1.0447 air-dry grams of untreated paper, 1.0302 air-dry grams of cold treated paper, and 1.0397 air-dry grams of hot treated paper. Each gram of paper was torn into pieces of an area of approximately 1 cm^2 and added to 25 mL of deionized water. After this, 20 mL of the acid was added. The solution was heated to boiling on a 150°C hot plate, then cooled to room temperature. Once cooled, pH was taken with a combination electrode. A burette was used to titrate the solution until it reached 4.95, equivalent to the pH of methyl red indicator used by the TAPPI standard. The solution was stirred manually throughout the addition of the base. The weight of each sample, initial pH, final pH, and amount of titrant were all recorded. The order in which the samples were tested was cyclical, so as to avoid

any possible effects in the results brought about by changes in titrant, atmosphere, etc. These tests were performed five times per book.

2.4.5 Surface pH Testing (TAPPI Method T 529 om-88)

Samples of the book were placed on a plastic surface to avoid any possible uptake by a backing material. The front side (odd-numbered) of the page was always used. Using a pipette, a single drop of deionized water was placed on the paper. The pipette tip was held slightly over the paper so as to avoid spreading the water over too large a surface area. After removing the buffer solution from the pH probe, it was secured above the page so that the tip touched the water droplet. After at least 10 minutes for equilibration, the electrode was removed vertically. Samples were taken from five evenly spaced locations across the page. Between each trial, the probe was resubmerged in buffer solution, which was monitored to ensure stable reading. Again, the testing order of the samples was done cyclically, so as to avoid any possible confounding variations. 10 samples were taken per book, five in a central location and five along the edge.

2.4.6 Molecular Mass of Cellulose

The paper specimens were treated following the standard protocol according to Potthast et al. (2015), which is based on solvent exchange from water to ethanol into DMAc. The samples were kept for 12 h in *N*,*N*-dimethylacetamide (DMAc), were dissolved in DMAc/LiCl 9% and diluted with DMAc prior to injection. The determination of molecular mass distribution was based on MALLS and refractive index in the DMAc/LiCl solvent system. The sampling positions for “immersed” and “not immersed”, as well as “middle” and “edge” areas are shown in Figure 1.

2.4.7 Electron Microscopy

Scanning electron microscopy (SEM) and related tests were carried out at the Analytical Instrumentation Facility (AIF) of North Carolina State University. Conventional SEM micrographs, offering relatively high magnification, were obtained using a Hitachi S3200 N variable pressure SEM equipped with an Oxford energy-dispersive X-ray spectrophotometer for elemental analysis. Specimens were coated with gold to increase the surface conductivity before obtaining the images.

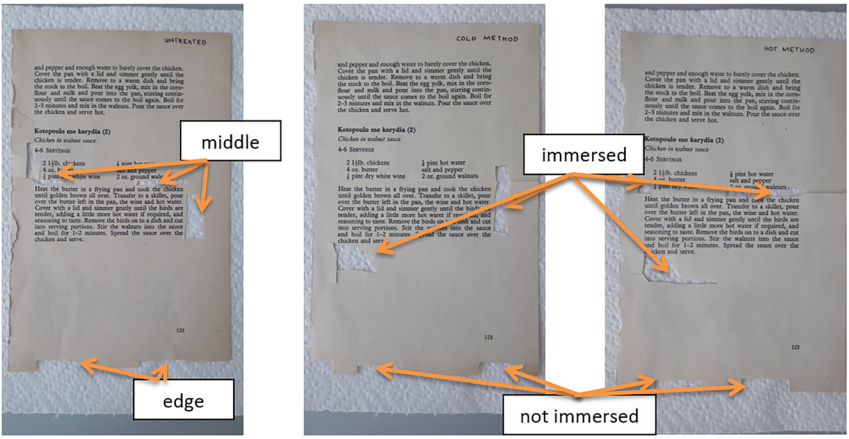

Figure 1: Photographs of Page 123 of Untreated (Left), Cold-Treated (Middle), and Hot-Treated (Right) Books, Indicating Regions That Had or Had Not Been Immersed During the Deacidification in 1967.

3 Results and Discussion

3.1 Brightness and Color

Results of brightness and color tests of the naturally aged paper specimens are shown in Table 2. Student's *t*-tests were carried out on the data pertaining to optical characteristics measured for the center section of the pages in the books. All of the deacidification treatments (both cold and hot) resulted in highly significant effects (p-values no larger than 3×10^{-5}, considering one-sided tests) for any of the comparisons. This means that the treated samples were brighter, had higher

Table 2: Results of Reflectance Measurements of Naturally Aged Paper with a White Backing.

Sample	*L**	*a**	*b**	Brightness
Untreated (center)	84.94 (0.45)	0.54 (0.50)	19.05 (0.85)	47.10 (1.45)
Cold (center)	85.92 (0.37)	−1.77 (0.46)	17.65 (0.56)	50.04 (0.99)
Hot (center)	86.03 (0.52)	−0.98 (0.82)	17.75 (0.99)	50.13 (1.72)
Untreated (edge)	84.52 (0.54)	0.72 (0.44)	19.24 (0.83)	46.28 (1.51)
Cold (edge)	85.59 (0.40)	−1.51 (0.43)	18.21 (0.43)	49.06 (1.19)
Hot (edge)	85.50 (1.02)	−0.74 (1.16)	18.55 (1.35)	48.58 (2.84)
Backing sheet	92.77 (0.18)	1.71 (0.02)	−5.48 (0.07)	90.07 (0.49)

Mean values; amounts in parentheses give the standard deviations (20 replicate measurements each).

lightness (L), lower (or even negative) redness (a), and lower yellowness (b) in comparison to the untreated paper after 52 years of natural aging.

Both the cold and hot treatment regimes employed by Smith in 1967 were shown to be effective. No significant differences between the results of cold versus hot treatment were evident in the data related to the optical properties.

Data corresponding to the edges of the pages provided confirmatory evidence. Visual observation of the pages suggested a tendency for deeper yellowing of the edges of sheets. However, as indicated by data in Table 2, this was not a strong tendency.

3.2 MIT Folding Endurance

Table 3 shows results for MIT folding endurance tests (TAPPI Method T 511), carried out in 2019 with a 0.5 kg load with paper strips equilibrated according to TAPPI test conditions (25°C, 50% relative humidity).

The deacidification treatments showed highly significant effects for folding endurance relative to the untreated books following 52 years of natural aging. Furthermore, the hot conditions of deacidification were revealed to have been much more effective than the cold conditions. The test results also confirm an expectation that the paper would be weaker in its cross-direction, in comparison to the direction of manufacture (machine direction). Notably, the effect of increased preservation of strength following deacidification treatment was evident for the CD specimens, though the numbers of folds before breakage were not as high as in the MD.

Figure 2 is based on a plot from the accelerated aging data reported by Richard Smith in 1970, except that data from Table 2 are entered into the plot as horizontal lines. As explained in the PhD thesis (Smith 1970), the diagonal lines plotted in Figure 2 are in general agreement with, but not identical to results of similar folding endurance tests performed in 1967 as part of the patent application process (Smith 1972).

As can be noticed, the intersections of the horizontal lines with the trend lines from 1967 accelerated aging tests show a profound lack of agreement between 52 years of natural aging time and the number of days of accelerated aging (TAPPI Method T 534). The crossing points for each pair of horizontal and diagonal lines

Table 3: Results of MIT Folding Endurance Tests of Naturally Aged Paper.

Sample	MD fold	CD fold
Untreated	3.4 (0.51)	3.75 (0.57)
Cold	22.2 (1.32)	6.55 (0.81)
Hot	33.2 (1.32)	8.00 (0.89)

Mean values; amounts in parentheses give the standard deviations (20 replicate measurements each).

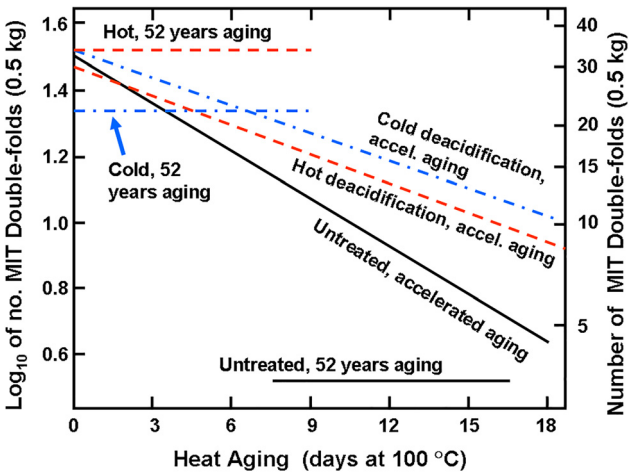

Figure 2: Comparison of Replotted Results for MD Folding Endurance From the Accelerated Aging Tests (1967; Shown As Diagonal Lines) with Results After 52 Years of Natural Aging (Horizontal Lines).

were all different from each other. For example, in the case of the untreated book, the number of double folds after 52 years of natural aging corresponded to approximately 21 days of 100°C aging. At the other extreme, the paper that had been deacidified under hot conditions did not show any strength loss at all, i. e. zero time of accelerated aging. The data for the cold deacidification treatment after 52 years was roughly equivalent to about seven days of accelerated aging.

3.3 Tensile Strength

Table 4 shows results of tensile strength tests based on TAPPI Method T 494. Significantly higher breaking lengths, resulting from the deacidification treatments, were observed only for the CD tests, not for the MD tests. However, in all cases the specimens that had been deacidified showed a higher percentage of stretch to breakage. Also, in all cases there were a highly significant increase in tensile energy absorption in the case of samples that had been deacidified in 1967.

3.4 Alkaline Reserve

As shown in Table 5, both sets of deacidification conditions were successful in imparting alkalinity to the paper in the treated books. Consistent with the results of

Table 4: Results of Tensile Strength Tests of Naturally Aged Paper.

Sample	Breaking length (km)	Stretch (%)	Tensile energy Absorption (J/m^2)
MD properties			
Untreated	3.37 (0.13)	0.898 (0.058)	11.85 (1.02)
Cold	3.32 (0.51)	1.190 (0.095)	17.45 (1.82)
Hot	3.28 (0.25)	1.093 (0.103)	16.31 (2.55)
CD properties			
Untreated	1.43 (0.10)	1.641 (0.208)	9.32 (1.80)
Cold	1.52 (0.06)	2.330 (0.321)	16.13 (3.03)
Hot	1.50 (0.06)	2.160 (0.174)	14.33 (1.66)

Mean values; amounts in parentheses give the standard deviations (20 replicate measurements each).

Table 5: Results of Alkaline Reserve Tests After Natural Aging.

Sample	Alkalinity ($CaCO_3$ %)	Alkaline reserve (mol/kg)
Untreated	−0.430 (0.179)	−0.086 (0.036)
Cold	0.373 (0.207)	0.075 (0.041)
Hot	1.411 (0.372)	0.282 (0.075)

Mean values; amounts in parentheses give the standard deviations (five replicate measurements each).

surface pH tests (see next), the paper from the untreated book had a negative alkalinity; in other words, it was shown to be acidic in nature and not falling within the scope of the test procedure. By contrast, the books that had been treated with magnesium methoxide in 1967 showed significant alkaline reserve amounts. In particular, the "hot" procedure, which is more consistent with commercially important practices, achieved a much higher level of alkaline reserve, as measured after 52 years of natural aging.

3.5 Surface pH

Tests of surface pH after 52 years of natural aging showed significant differences depending on the type of treatment or non-treatment of the books in 1967. Table 6 compares the results obtained in 2019 with those obtained fresh in 1967 (no accelerated aging and about three years after the paper was made).

This confirmed the expected results of the treatment, as the pH was significantly different. The pH averaged 4.0 for untreated, 7.1 for cold treated, and 7.4 for hot treated.

Table 6: Results of Surface pH Tests of Naturally Aged Paper (2019) and Fresh (1967) Paper.

Sample	1967 (fresh)	2019 (after 52 years)
Untreated	4.3–4.4	4.0 (0.12)
Cold	10.3–10.5	7.1 (0.80)
Hot	9.5–9.8	7.4 (1.17)

Mean values; amounts in parentheses give the standard deviations (five replicate measurements each).

3.6 Molecular Weight Distribution of Cellulose

Results for the molecular weight distribution of the cellulose polymer in the paper specimens are summarized in Table 7. The headings in Table 7 correspond to the number-average molecular mass (M_n), the weight-average molecular mass (M_w), the *Z*-average molecular mass (M_z), and the dispersity (M_w/M_n). Repeat tests for the same conditions generally showed agreement to be within 7% of the average value. On this basis there was a significantly higher molar mass of the cellulose within the books that had been deacidified before they had been stored for 52 years.

Figure 3 shows results related to the molecular mass of cellulose in the paper specimens. Based on Figure 3, a slightly better stabilization was achieved when using the cold procedure compared to the hot variant, which is not in agreement with the double fold test results. The cold treatment retained 37% more weight-average molar mass compared to 32% for the hot variant. The non-immersed part for the hot treatment showed also a slight stabilization compared to the non-treated paper (+13.5% for the hot treatment). This value was slightly lower for the cold treatment (+7.7%). In both cases this indicates that some alkali also reached the non-immersed parts, and this was more pronounced for the hot treatment.

Table 7: Results of Molar Mass Analysis of Naturally Aged Paper (2019). Statistical Moments of the Molecular Weight Distribution are Given in kg/mol (Average of Two Separate Measurements).

Sample	M_n	M_w	M_z	$Đ(M_w/M_n)$
Untreated				
Middle	22.2	184.9	581.5	8.3
Edge	37.5	193.8	552.9	5.2
Cold				
Immersed	25.7	294.2	883.1	11.6
Not immersed	31.3	210.0	577.2	6.81
Hot				
Immersed	24.2	270.9	825.0	11.3
Not immersed	41.0	224.1	600.0	5.5

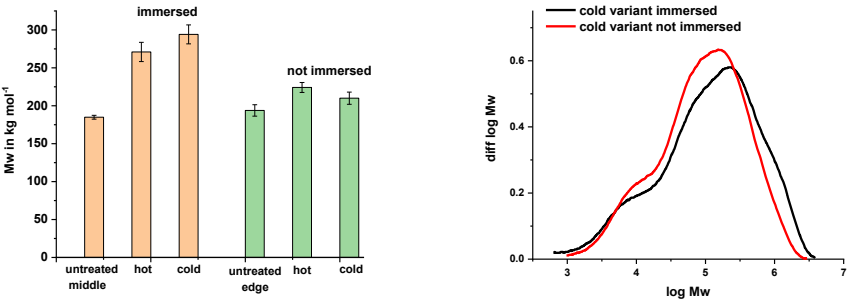

Figure 3: (a) Comparison of M_w Data for the Different Treatments. Error Bars are Average Deviations of Two Measurements. (b) Molecular Weight Distribution for the Immersed Versus the Non-Immersed Cold Treatment.

Figure 3b shows the molar mass distribution. The mass deacidification treatment protected mainly the long cellulose macromolecular chains that are essential for macroscopic paper strength, which is in agreement with literature data.

The findings shown in Figure 3 can provide evidence relative to the speed of natural aging. One can assume, as a first approximation, that the cold deacidification treatment locked the status of the paper from 52 years ago and that subsequently it did not degrade much compared to the untreated variant. This assumption is supported by the 2019 MIT folding test results, which were similar to what was measured back in 1967. The untreated book paper corresponds to what would be expected for natural aging of this paper. Applying the Ekenstam Eq. (5, left), one can calculate the half-life DP (right) of this paper as $t_H = 87$ years; i. e. after 87 years the DP of the paper was only half of its original value. This does not imply that the paper had reached a critical stage, which is usually 3–4 times halving of the DP (DP × 0.5 × 0.5 × 0.5, etc.), bringing the paper down to full loss of mechanical strength.

To see how realistic this value is, one can use the data of Jeong et al. (2014), in which the value of t_H was determined for Hanji paper. The starting point of aging in his case was a fresh Hanji paper produced according to historic recipes. Tests of these newly formed specimens provided an initial value of degree of polymerization, i. e. $DP_{o,}$ – a status which is usually not accessible. Based on that number, the natural speed of aging could be determined by comparison to naturally aged Hanji paper after about 500 years. In order to get a correlation to other papers or pulps, the Korean Hanji was subjected to accelerated aging together with a number of test papers, including a hardwood sulfite pulp and a groundwood paper. The groundwood pulp aged 5.3 times faster than Hanji, and the chemical hardwood sulfite pulp aged 2.8 times faster. With $t_H = 514$ years for the Hanji paper, this comes down to 97 years for groundwood and 183

years for the sulfite pulp. The error of this approximation is certainly large due the different pulp types and a large overall error, but still the data fit surprisingly well to the 87 years of half-life of the book considered in the present study.

$$kt = \frac{1}{\mathrm{DP}_t} - \frac{1}{\mathrm{DP}_0} t_H = \frac{\left(\frac{1}{(\mathrm{DP}_0/2)} - \frac{1}{\mathrm{DP}_0}\right)}{k} = \frac{1}{\mathrm{DP}_0 k} \tag{5}$$

3.7 Electron Microscopy

Scanning electron microscopy, carried out in the field emission mode, together with an elemental analysis module, was used to collect the elemental information provided in Figure 4. As shown, there was no magnesium detected in the default paper specimen taken from the untreated book. By contrast, a distinctive peak for Mg was evident in results corresponding to a deacidified specimen of paper (hot condition). Essentially the same results, showing the presence of Mg, were obtained when evaluating a specimen from the book that had been subjected to the cold treatment in the course of deacidification (not shown). These results confirm that a detectable amount of Mg was contributed to the paper in the course of the deacidification treatment.

An elemental map was obtained for magnesium corresponding to an SEM micrograph for the deacidified paper (hot) (see Supplementary material). The results indicate a relatively uniform distribution. Notably, there was no evidence of Mg-

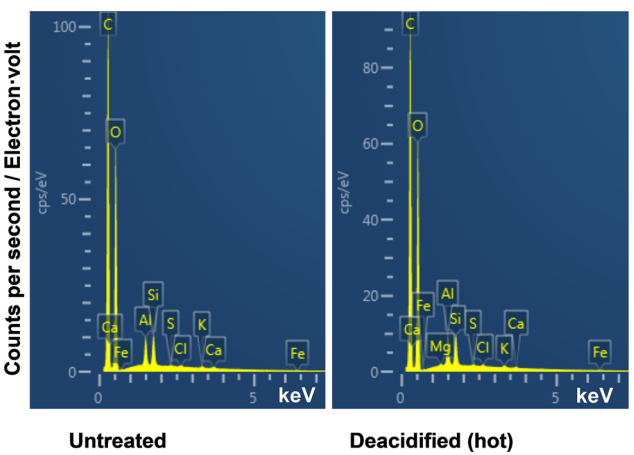

Figure 4: Metal Elemental Content of Paper From Untreated (Left) and Hot-Deacidified (Right) Books After 52 Years of Natural Aging.

containing particles larger than about 1 μm. Close inspection of the original version of this figure showed some sparse evidence of higher amounts of Mg signal coming from what appeared to be particles having diameters in the range 2–10 μm. These are tentatively attributed to the presence of talc, which is commonly added during the manufacture of paper in order to reduce the tackiness of wood pitch (Benecke et al. 2009). Another likely source of such Mg-containing particles could be the byproducts from residual droplets of magnesium methoxide remaining on the paper surface following removal and evaporation of the chlorofluorocarbon carrier liquid.

Figure 5a, b are SEM micrographs at two levels of magnification obtained for a specimen from untreated paper. A noticeable feature of these micrographs is the presence of cellulosic fibers, which cross the plane of view in various directions. Cellulosic fibers of the types commonly used in the preparation of book papers have diameters of approximately 20–30 μm. After refining, some of the cellulosic material is likely to be present as smaller fibrils. Also visible in the micrographs are clay particles, which are notable for their flat faces and relatively straight edges. Clay particles can have diameters in the range from less than one to about 10 μm.

Figure 6a, b are SEM micrographs corresponding to a deacidified paper specimen. The conditions of testing were identical to those of the previous figure. No characteristic differences were detected by the authors, depending on whether or not deacidification had been carried out of the paper.

4 Mechanistic Implications

It is rare to be able to compare the results of accelerated aging tests with natural aging of exactly the same samples over a time span as long as 52 years. The earlier

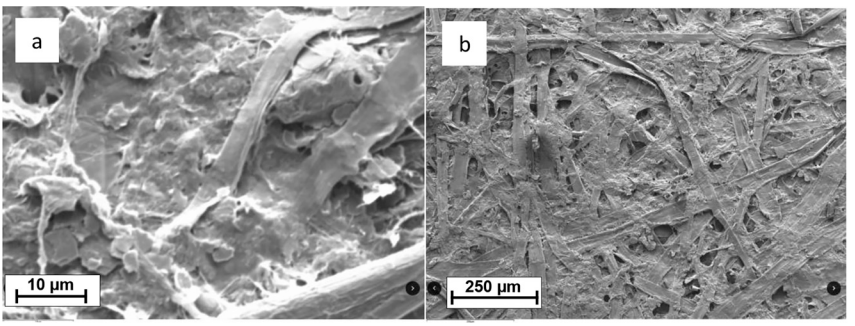

Figure 5: Scanning Electron Micrographs of the Surface of Paper From an Untreated Copy of the Book as the Two Magnifications Indicated.

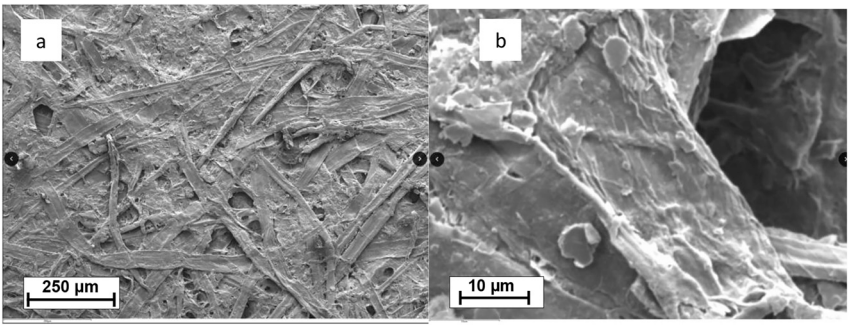

Figure 6: Scanning Electron Micrographs of the Surface of Paper From a Hot-Deacidified Copy of the Book as the Two Magnifications Indicated.

work reported by Wilson and Parks (1980) laid a foundation by showing a strong correlation between the results of accelerated aging and 37 years of natural aging of a diverse set of paper specimens. However, none of those specimens had been deacidified. Smith's thesis work (Smith 1970, 1972) included accelerated aging tests, comparing paper from deacidified and untreated books. The results implied a finite, but decreased rate of loss in folding endurance when comparing the deacidified paper with the untreated paper. By contrast, the folding endurance tests carried out in 2019 on naturally aged paper from the "hot"-deacidified book showed no change at all in folding endurance in comparison to the tests carried out on the untreated books in 1967. These contrasting results suggest that the accelerated aging assay was somehow unfair to the deacidified paper, not being able to predict that it would fully halt at least one aspect of paper aging. The present results thus suggest the need for caution when using accelerated aging tests followed by folding endurance tests to evaluate the performance of paper deacidification treatments.

Because only one type of accelerated aging test was applied to the specimens in 1967, conditions similar to the TAPPI "dry heat" method (T 453), only limiting conclusions can be drawn regarding the selection of such test methods. According to Potthast and Ahn (2017), the dry accelerated aging conditions are slow in their effects on the paper and ought not to be regarded as providing reliable information regarding natural aging. It is notable, however, that even the "dry heat" conditions accelerated the observed loss in folding endurance well beyond the observed level of zero loss in folding endurance after 52 years of natural aging. It appears that even when only a very minor amount of moisture was present in the dry paper, the heating still was able to induce destructive effects on the untreated acidic paper.

The overall results of both the 1967 evaluations and the recent evaluations of the book – comparing untreated and deacidified copies – tend to support the initial mechanistic assumption of the inventor, who assumed that the magnesium methoxide would react with and neutralize the acidic compounds in the paper, thus greatly decreasing a prime cause of paper's deterioration during storage (Smith 1972). Evidence regarding the chemical aspects of the treatment, as collected in a review article (Hubbe et al. 2018), also appear consistent with the present findings.

5 Conclusions

Evaluation of paper specimens after 52 years of natural aging demonstrated the effectiveness of non-aqueous deacidification treatments. Books that had been deacidified by immersion in a chlorofluorocarbon solution of magnesium methoxide, followed by drying and air-equilibration, showed either no decline or a much reduced decline in folding endurance compared to similar tests on an untreated book that likewise had been stored for 52 years.

Accelerated aging tests that were carried out in 1967 did not provide an accurate prediction of natural aging. Paper specimens that had been deacidified by the "hot" procedure (drying at 100°C for 4 h before treatment with dilute magnesium methoxide in chlorofluorocarbon, followed by drying and equilibration in ambient air) were predicted by the accelerated aging tests to show a decline in the logarithm double folds equal to about 2/3 of the corresponding decline in the untreated books. However, according to evaluation of the naturally aged specimens, the book treated by the "hot" procedure did not show any decline at all in folding endurance in comparison to tests performed in 1967.

No tests of cellulose molecular mass were carried out in 1967. Only the folding endurance test results and pH results were carried out both in 1967 (fresh and accelerated aging) and in 2019 (natural aging). It has been argued that the hydrolytic cleavage of glycosidic bonds within cellulose molecular chains can explain much of the observed aging effects of acidic paper specimens (Potthast and Ahn 2017). If cellulose molecular mass tests had been carried out on the samples in 1967, the repetition of such tests in 2019 would have provided especially valuable information.

The fact that 52 years of natural aging did not change the folding endurance of the paper that had been subjected to the "hot" deacidification suggests that the hydrolytic cleavage of cellulose macromolecular chains had been effectively blocked. If it is further assumed that such blockage had been almost completely

effective, then the rate of hydrolysis can be estimated for the case of the untreated copy of *Cooking the Greek Way*. As shown earlier in this article, the half-life of the untreated copy was estimated as 87 years, based on such an assumption.

Experimental evidence, as follows, confirmed that the deacidification treatments carried out in 1967 had been successful. The surface pH of the deacidified paper, after 52 years of storage, was measured as 7.1–7.4, while that of the untreated book was 4.0 (compared to about 4.3 in 1967). The alkaline reserve values of the treated books were in the range 0.07–0.28 mol/kg of paper (0.37–1.41% expressed as $CaCO_3$ equivalents), whereas the untreated book had no alkaline reserve. Molar mass analysis clearly showed the positive effects of deacidification for both treatments tested. The cold version was even slightly more successful in preserving the long cellulose chains, which are essential for retaining mechanical properties of the paper.

X-ray fluorescence tests, using scanning electron microscopic analysis, showed the presence of magnesium in the treated specimens but not in paper from the untreated book. Also, preservation of folding endurance and the superior tensile strength, stretch to breakage, and higher tensile energy absorption compared to the untreated paper after 52 years of natural aging indicate the success of the deacidification treatment.

Electromicroscopic examination of the paper surfaces, comparing deacidified paper versus untreated paper, showed no apparent differences. The main visible features in the micrographs were consistent with the presence of cellulosic fibers, some finer cellulosic material, such as fibrils, and clay particles.

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Supplementary Material: This article contains supplementary material (https://doi.org/10.1515/res-2020-0006).

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Accelerated Aging of Deacidified and Untreated Book Paper in 1967 Compared with 52 Years of Natural Aging

SUPPLEMENTARY INFORMATION

Full set of molecular mass results:

	NAWAROS ID	Mn [kDa]	Mw [kDa]	Mz [kDa]	Dispersity Đ [Mw/Mn]	Reg [µmol/g]	dn/dc [mL/g]	calculated mass [µg]
Untreated								
middle	MHUnt1	22.04	183.10	576.5	8.31	45.37	0.136	185
middle	MHUnt2	22.39	186.70	586.4	8.34	44.66	0.136	225
average		**22.22**	**184.90**	**581.5**	**8.32**	**45.02**		
edge	UntNO1	35.16	199.40	576.8	5.67	28.44	0.136	284
edge	UntNO2	40.33	188.30	529.0	4.67	24.80	0.136	220
average		**37.75**	**193.85**	**552.9**	**5.17**	**26.62**		
Cold method								
immersed	MHCOL1	23.05	303.00	932.9	13.14	43.38	0.136	141
immersed	MHCOL2	28.35	285.30	833.3	10.06	35.27	0.136	214
average		**25.70**	**294.15**	**883.1**	**11.60**	**39.33**		
not immersed	COLNO1	27.17	204.30	591.5	7.52	36.81	0.136	213
not immersed	COLNO2	35.42	215.70	562.8	6.09	28.23	0.136	244
average		**31.30**	**210.00**	**577.2**	**6.81**	**32.52**		
Hot method								
immersed	MHHOT1	21.18	262.00	824.8	12.36	47.21	0.136	152
immersed	MHHOT2	27.26	279.90	825.1	10.26	36.68	0.136	197
average		**24.22**	**270.95**	**825.0**	**11.31**	**41.95**		
not immersed	HOTNO1	38.72	228.80	636.9	5.91	25.83	0.136	250
not immersed	HOTNO2	43.30	219.50	562.9	5.07	23.09	0.136	260
average		**41.01**	**224.15**	**599.9**	**5.49**	**24.46**		

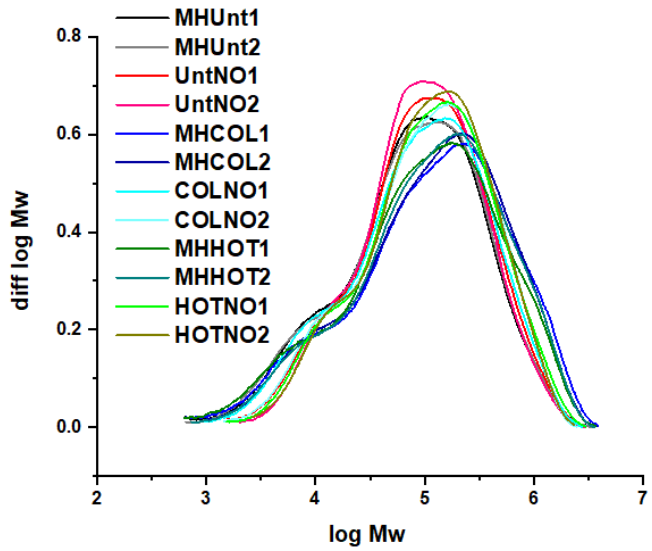

Figure 1: Molecular weight distribution of all samples

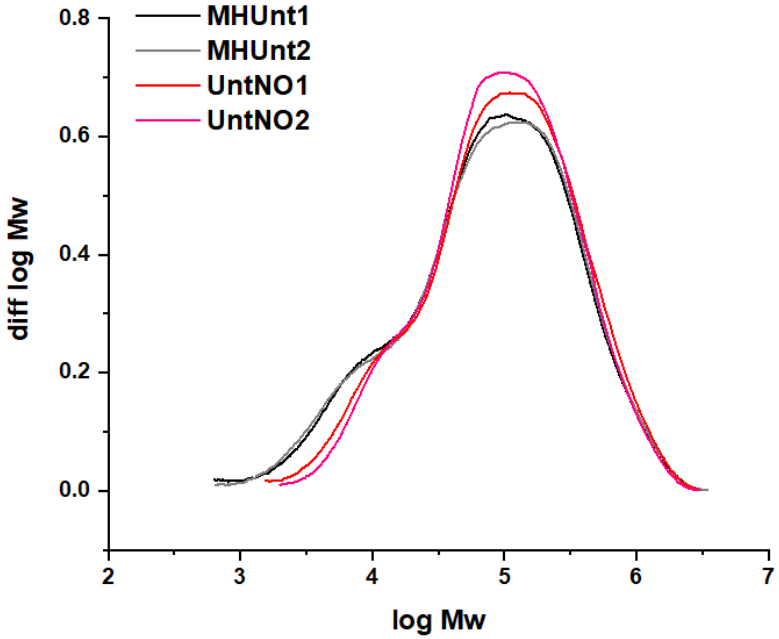

Figure 2: Molecular weight distribution of samples untreated

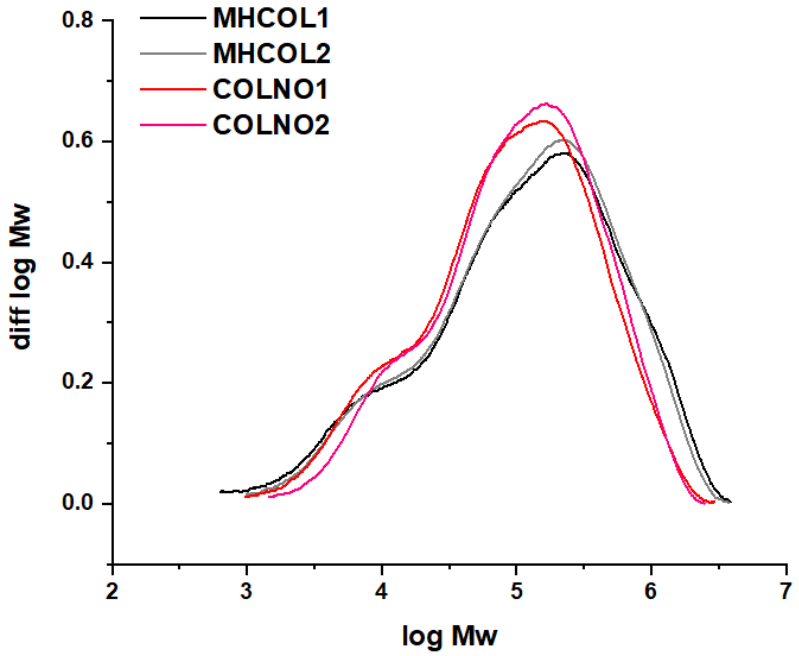

Figure 3: Molecular weight distribution of samples after “cold method”

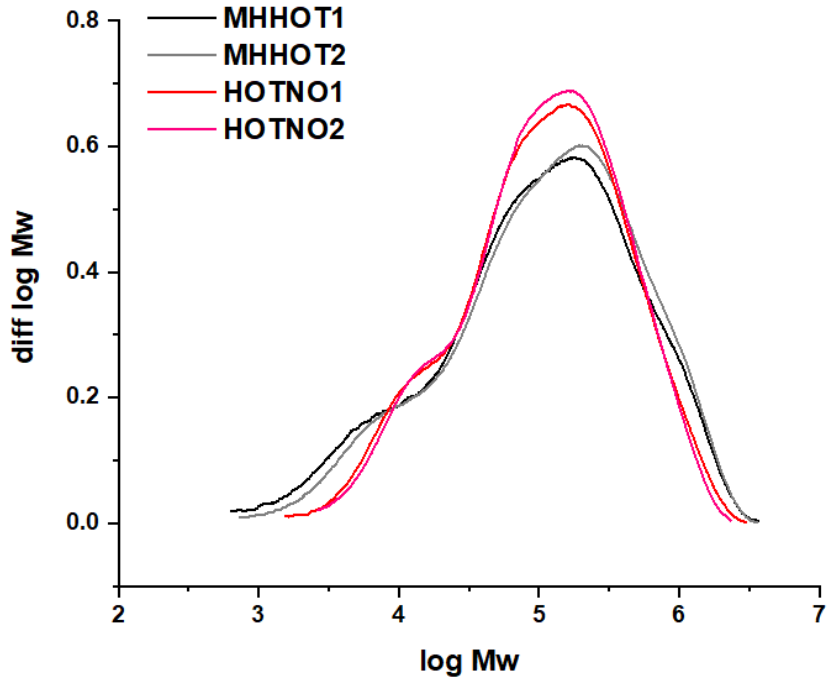

Figure 4: Molecular weight distribution of samples after “hot method”

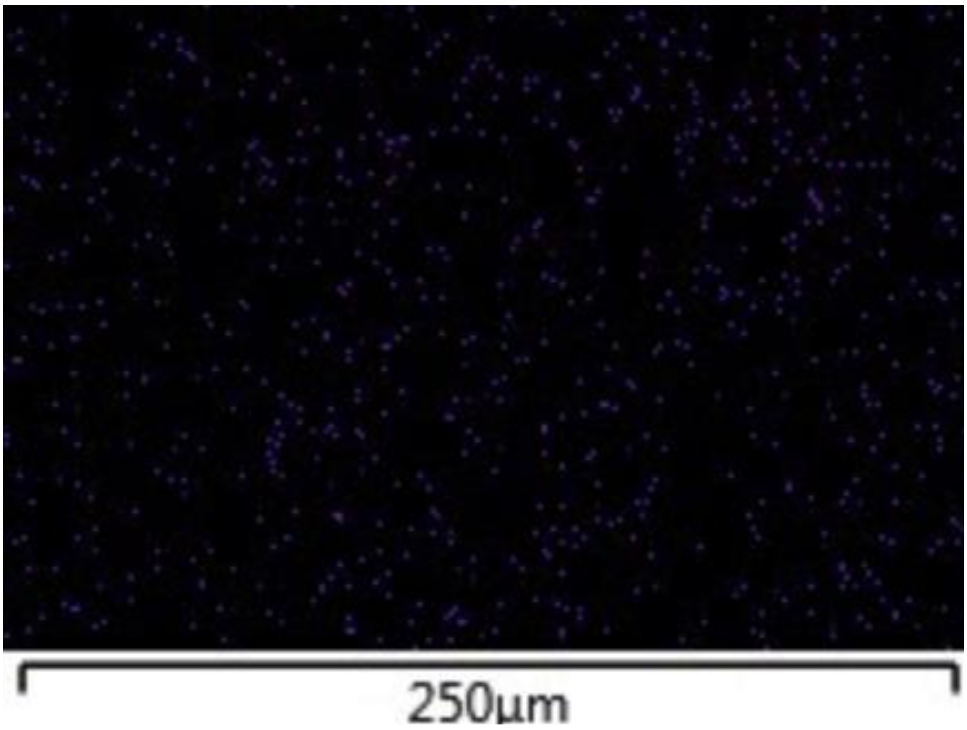

Figure 5: Magnesium elemental map (representative view)