Evaluation of Conventional Paper Deacidification Processes: An Analytical Study

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Abstract:

Acidity is a topic of great concern to paper conservators as it is one of the most important causes of damage in paper-based objects. Early in the 19th century, all paper was manufactured from old linen and cotton rags. However, from the mid-19th century onwards, increasing demand of paper allowed the widespread of wood pulp as the raw material for paper making. The change from rag and linen to wood pulp *is the most significant factor in* paper deterioration. *Wood pulp paper, with its short, weak fibers and high acidity, causes serious problems for libraries and archives having to preserve materials that rapidly become brittle. Paper is susceptible to acid deterioration through contamination by inherent acidic components, by acidic materials used in there manufacture, and by atmospheric pollutants. The first visible evidence of such deterioration is discoloration and at the same time the paper loses its mechanical strength. These cases may greatly benefit from deacification. It was the aim of this research to study the effects of common deacidification treatments on the chemical and physical properties of paper. The following deacidification treatments were investigated: barium hydroxide, calcium carbonate, and magnesium carbonate. Changes promoted in paper, as a result of these treatments, were measured and registered based on the consideration of the following criteria: changes in the surface of the paper through visual inspection, changes in the chemical structure of the cellulose through Fourier transform infrared spectroscopy (FTIR), changes in color through spectrocolorimetric measurements; changes in pH of the paper, and changes in the mechanical properties of paper. Measurements were carried out before and after the treatments. Test results gave an indication of the benefits and potential problems of each treatment.*

Keywords: *Paper; acidity; yellowing; embrittlement; deacidification; pH value; FTIR, color change; tensile strength, elongation ratio.*

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1. Introduction:

The degradation of paper objects is important particularly in archives, libraries and museums where aging reduces the mechanical properties and deteriorates optical properties of stored papers, books photographs, and other artefacts [1]. After the invention of printing, paper demand consistently increased and the methods of papermaking radically changed. In the middle of the 19^{th} century, paper making from rags was replaced by the use of wood pulp, producing more chemically reactive paper sheets, subjected to hydrolytic, oxidative, and thermal degradation [2]. Acidity of paper has been identified as the most important intrinsic factor that promotes the aging of paper materials [3]. Cellulose, the primary constituent of paper fibers, is a polysaccharide consisting of linear chain of several hundred to over nine thousand glucose units which are linked together by 1-4 glycosidic oxygen bonds [4]. Over prolonged periods, paper undergoes inevitable ageing processes that cause the degradation of cellulose: these processes can involve acid substances and moisture (acid hydrolysis), oxidative agents and the atmospheric O_2 (oxidation), micro organisms (biodeterioration), or light (photodegradation) [5]. However, it has been shown that acid-catalyzed hydrolysis is the most dominant degradation path leading to considerable losses in degree of polymerization [1]. This process degrades cellulose by random scission of the hemi-acetal links leading to hydrolyzed cellulose, a material analogous of cellulose, but with shorter chain length [6]. The decrease of the degree of polymerization affects all the mechanical properties [3]. It also generates carbohydrate fragments which oxidize forming carboxylic acids. These acids enhance the acidity of paper and thus initiate an auto-catalytic degradation cycle [1]. Additional degradation processes are related to the oxidative degradation f cellulose, primarily induced by the presence of oxygen in the atmosphere and the thermal degradation [2]. The oxidation of cellulose involves the primary and secondary hydroxyl groups of the pyranose ring which results in the creation of carbonyl (C=O) and carboxyl groups (-COOH). These groups are chromophores and their creation is one of the reasons paper yellows as it ages [7]. The compounds that are produced from the degradation of the lignocellulosic matrix are mainly carbonyl compounds. During degradation of the lignocellulosic part, mainly formic acids, acetic acid and formaldehyde and a variety of acids and aldehydes are produced. Acidity is both the consequence of accumulation of acids

in paper during degradation process and the result of acids introduced into paper during production, and it is known that acidic paper are less stable compared to neutral and alkaline ones [1]. The deacidification of paper is known to reduce this deterioration and extend the useful life of such materials by several times [6]. Deacidification is the term used for a chemical treatment in paper conservation, which involves the neutralization of the acids present in paper and the deposition of an alkaline compound, commonly referred to as alkaline reserve, to prevent, or at least delay, further acidification [8]. A correct deacidification process should produce the complete neutralization of the acidic paper and thermodynamically stable side products, which act as an alkaline reservoir, keeping the pH around 8-9. Many different techniques and products have been developed [2]. In this paper, the following deacidification treatments were investigated: barium hydroxide, calcium carbonate, and magnesium carbonate. Changes promoted in paper, as a result of these treatments, were measured and registered based on the consideration of the following criteria: changes in the surface of the paper fibers through digital imaging, changes in the chemical structure of the cellulose through Fourier transform infrared spectroscopy (FTIR), changes in color through spectrocolorimetric measurements; changes in pH of the paper, and changes in the mechanical properties of paper. Measurements were carried out before and after the treatments. Test results gave an indication of the benefits and potential problems of each treatment.

2. Materials and Methods

2.1. Material

Calcium carbonate, magnesium carbonate and barium hydroxide were supplied by Trading Dynamic Co. Methanol was supplied by ADWIC. Tap water was used for all experiments and all chemicals were of analytical grade.

The paper used for the experiments was wood pulp paper. This particular paper was selected for the experimental work because it resembles historic paper.

2.2. Treatments and accelerated aging

A total of 5 samples were utilized. Two samples remained untreated as a reference. The remaining three samples were treated by brush with 0.5%, 2%, and 2% of

barium hydroxide in methanol, calcium carbonate in tap water, and magnesium carbonate in tap water, respectively.

Accelerated aging was applied to the treated samples and one reference sample in a a Binder dry oven at a temperature of 80 °C and 65% RH for 5 days, which is equivalent to aging of paper under natural conditions for 25 years. The aging procedure was in conformance with the ISO 5630-3:1996 standard [9].

The samples were all numbered and labeled on the reverse using a graphite pencil according to the treatment used as shown in table 1.

Table 1: Sample numbers

Test	Sample number
Reference sample	R
Aged reference sample	AR
Barium hydroxide in methanol (0.5%)	Ba
Calcium carbonate in tap water (2%)	Ca
Magnesium Carbonate in tap water (2%)	Mg

2.3. Analysis

The surface, optical, mechanical and chemical properties of the tested paper samples were determined as follows:

- Visual inspection.
- pH was measured by a cold extraction method according to TAPPI T 509 at room temperature using a pH meter.
- Mechanical behavior of the samples (i.e. tensile strength and elongation %) were studied using the dynamometer produced by SDL ATLAS, H5KT. The samples were cut in the machine direction to strips of 2 cm × 10 cm.
- FTIR spectra of paper samples were measured on a Nicolet 380 FT-IR Spectrometer, in the frequency range of 4000 - 400 cm^{-1}, in reflectance mode.
- The color of the samples was measured with a Optimatch 3100® from the SDL Company. All samples were measured in a visible region, i.e., a wavelength range from 400-700nm, with an interval of 10nm using a D65 light source and an observed angle of 10 degrees. The colorimetric coordinates L*, a*, and b*of

the CIE L*a*b* color space were used to express color change. The CIELAB color space is organized in cube form. The L* axis runs from top to bottom. The maximum for L* is 100, which represents white. The minimum for L* is zero, which represents black. The a* and b* axes have no specific numerical limits. Positive a* is red. Negative a* is green. Positive b * is yellow. Negative b* is blue [10].

All measurements were made before and after treatment and compared to that of the aged control sample.

3. Results and Discussion

3.1. Visual Inspection

All samples show minor wrinkling in the case of aqueous treatments (i.e. calcium carbonate and magnesium carbonates. Good results were obtained in the case of barium hydroxide, a non-aqueous treatment ***(Fig. 1)***.

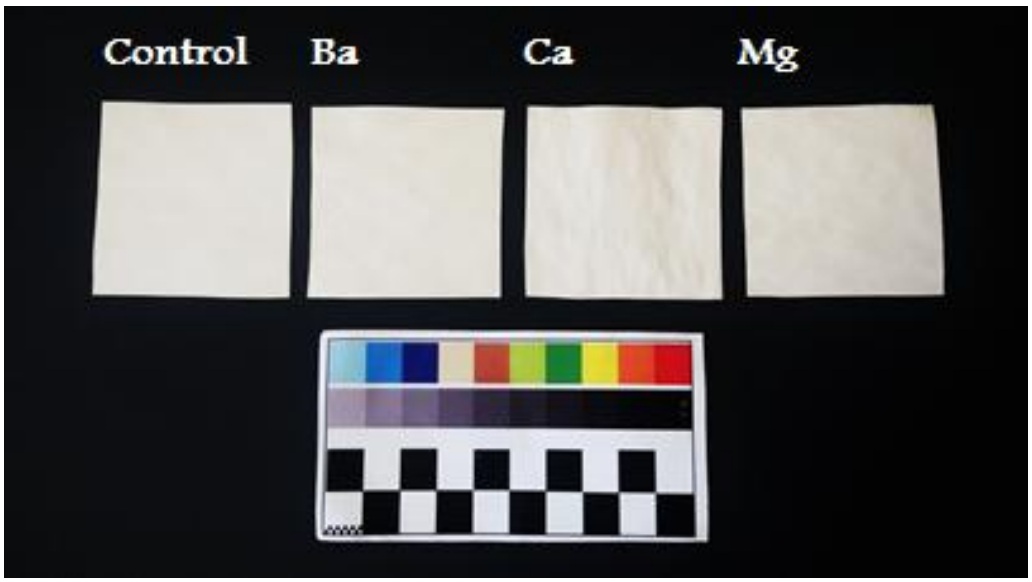

Fig. 1. Treated samples after accelerated aging compared to aged control sample.

3.2. pH Measurement

pH data of all the samples were in mild alkaline medium. The lowest pH was for paper samples treated with barium hydroxide with a value of 7.01. Samples treated with magnesium also provided very close pH reading of 7.64. The highest pH data (9.04) was observed on samples treated with calcium carbonate.

3.3. Mechanical Properties

Tensile strength and elongation more nearly approaches a fundamental measurement than other conventional strength measurements on paper [11]. The values of tensile strength and their decrease in percentage are shown in table 2, ***(Fig. 2)***, and ***(Fig. 3)***. The results reported are the average of five measurements with standard deviation. The results obtained indicate that the smallest decrease in tensile strength was caused by barium hydroxide in methanol. A solution of calcium in tap water caused the highest decrease in tensile strength compared to the reference sample; the values of elongation indicate that the paper samples treated with barium hydroxide in methanol were less flexible than those treated with magnesium carbonate and calcium carbonate in tap water.

Table 2: Tensile strength and elongation values of treated aged samples

Sample No.	Elongation (%)	Tensile Strength (N)
AR	1.55	85.06
Ba	1.44	79.2
Ca	1.73	72.3
Mg	1.68	74.7

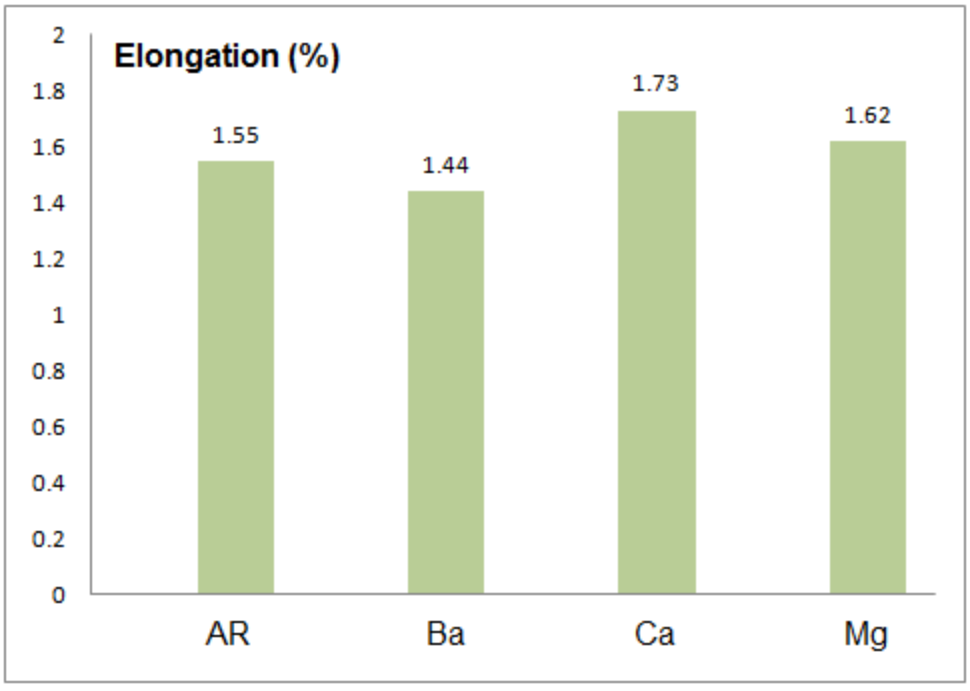

Fig. 2. Values of elongation resulting from tested deacidification treatments

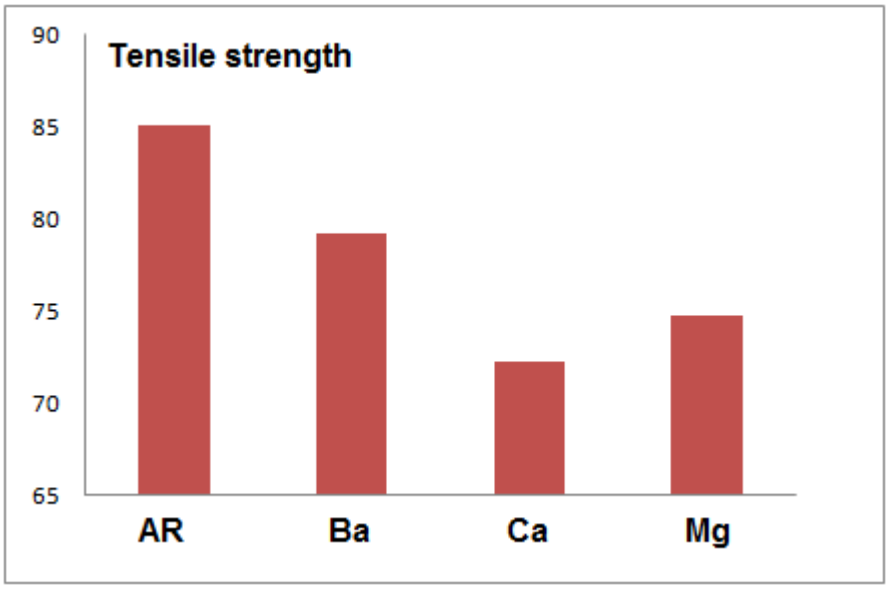

Fig. 3. Values of tensile strength resulting from tested deacidification treatments

3.4. FTIR Analysis

Although FTIR spectra of paper are quite complex, some absorbtion frequencies are illustrative of the deacidification process. The blue spectrum which represents the reference sample (AR) gave rise to the carboxyl group (COOH) at 3100 – 3400 cm^{-1} and carbonyl group (C=O) at around 1620-1650 cm^{-1}, which indicates the occurrence of oxidation, a degradation process that occurs due to paper acidity. We observed in the the barium hydroxide spectrum, represented in red, a decrease in the broading of the carboxyl group and a decrease in the intensity of the carbonyl group ***(Fig. 4)***. Similar results appeared in the case of the magnesium carbonate solution spectrum ***(Fig. 5)***. These results indicates minor deacidification of the paper samples. Good results appeared in the case of the sample treated with the calcium carbonate solution. The spectrum shows that the carboxyl group, a product of degardation, has disappeard and the OH band which is characteristic for cellulose has been recovered. There is also an obvious decrease in the intensity of the carbonyl group, another product of degradation ***(Fig. 6)***.

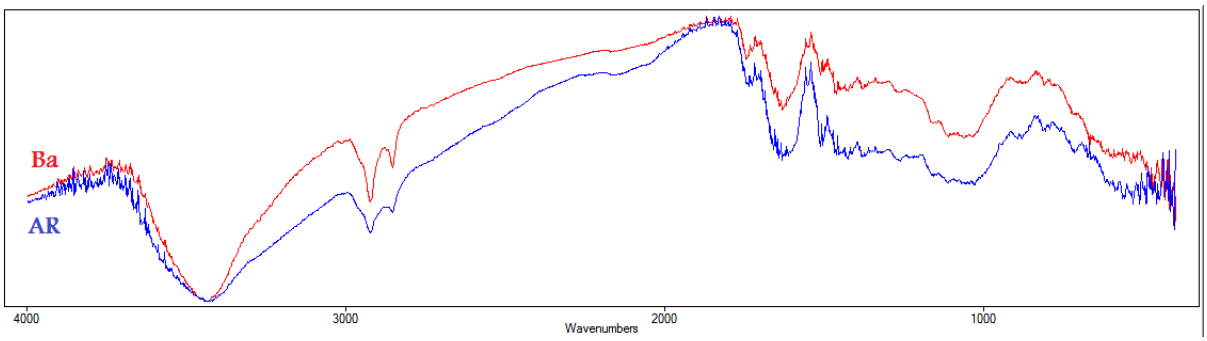

Fig. 4. FTIR spectrum of the sample treated with barium hydroxide in methanol compared to the aged control sample.

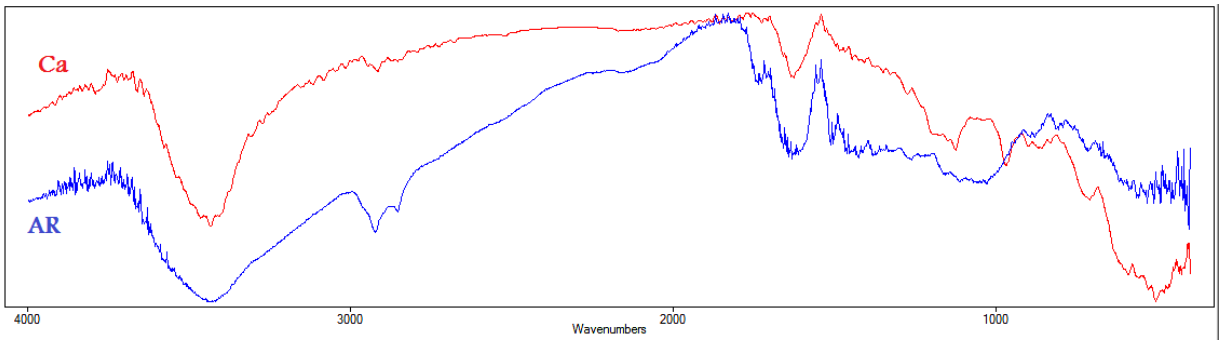

Fig. 5. FTIR spectrum of the sample treated with calcium carbonate in water compared to the aged control sample.

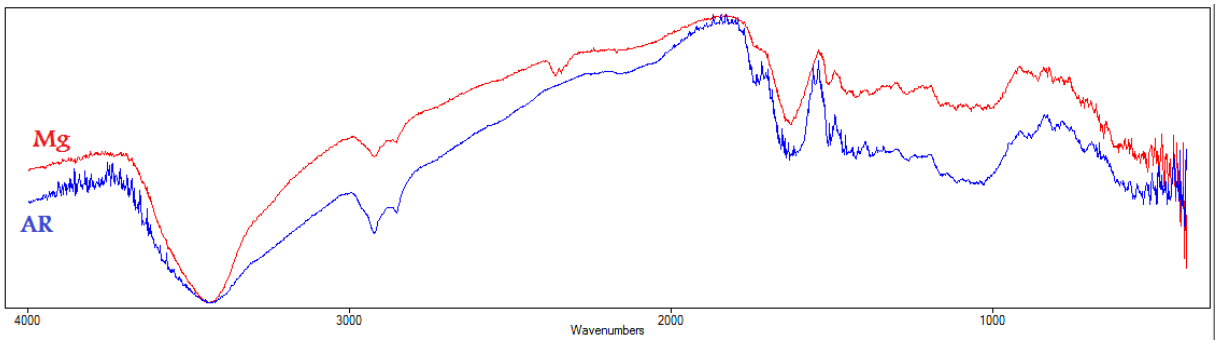

Fig. 6. FTIR spectrum of the sample treated with magnesium carbonate in water compared to the aged control sample.

3.5. Colorimetric Measurements

An important issue of conservation treatments is the impact of the treatment on the original color of the object treated. For this reason it is important to minimize the

color change due to the addition of a new material [12]. The parameters L*, a*, b* and the total color difference ΔE are represented in table 3.

Table 3: Colorimetric coordinates of CIE L*a*b* color space (each value is the average of 3 reading on each sample)

Sample	L*	a*	b*	ΔE
Reference (aged and untreated)	90.05	0.10	12.59	
Barium hydroxide in methanol (0.5%) (unaged, treated)	89.71	0.14	9.54	
Barium hydroxide in methanol (0.5%) (aged, treated)	89.17	0.22	13.62	4.12
Calcium carbonate in tap water (2%) (unaged, treated)	89.53	- 0.23	10.97	
Calcium carbonate in tap water (2%) (aged, treated)	88.98	0.07	13.17	2.29
Magnesium carbonate in tap water (2%) (unaged, treated)	90.30	0.05	9.82	
Magnesium carbonate in tap water (2%) (aged, treated)	89.14	0.04	13.23	3.60

All aged treated samples show lower L* values than the aged reference samples, with the values 89.17, 89.98, 89.14 for barium hydroxide, calcium carbonate, and magnesium carbonate, respectively. Barium hydroxide in methanol showed the least darkening compared to the aged reference sample. Color change in tested samples is expressed by the ΔE parameter. ΔE indicates the difference between each chromatic coordinate (ΔL*, Δa* and Δb*) in treated aged reference sample, treated unaged samples, and treated aged samples. ΔE values must not exceed 3 since values higher than 3 and lower than 6 can be visually detected (**Limbo and Piergiovanni, 2006)** [13]. In this study, the values of ΔE increased beyond 3 in all treatment except in the case of calcium carbonate, with ΔE values of 2.29.

4. Conclusions

The analysis of the changes resulting from accelerated aging of treated samples led to the following concluded remarks:

- Visual inspection revealed that the paper sample treated with barium hydroxide was able to preserve the topography of the paper surface.

- Calcium carbonate treatment increased the pH value to 9.04, which indicated that a complete neutralization of the acidic paper has been achieved.
- Non-aqueous treatments, represented in barium hydroxide in methanol, better preserved the mechanical properties of the paper, compared to calcium carbonate and magnesium carbonate.
- According to FTIR analysis, calcium carbonate was able to eliminate acidity and increase the alkalinity of the paper.
- Color alteration was the least in the case of the calcium carbonate, an important issue of conservation treatments.

According to the obtained results, the authors recommend treating acidity in paper-based objects with a 2% solution of calcium carbonate in water. Non-aqueous treatments (i.e. barium hydroxide), which are suitable for water-soluble media requires further studies.

5. References

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