The Immediate Impact of Aqueous Treatments on the Strength Properties of Paper.

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1. Introduction

Washing and aqueous deacidification dominate paper conservation literature and practice, since they are considered fundamental treatments that simultaneously clean and stabilize paper chemically. Hey (1979)[1], Wilson et al (1981)[2], Calvini et al (1988)[3], Bredereck et al (1990)[4], Lienardy et al (1990a)[5], Hanus (1994)[6], Kolar et al (1996)[7], Sistach (1996)[8], Zappala (1997)[9], Bansa (1998)[10] and many more report on the use of various paper deacidification agents (mainly calcium hydroxide $Ca(OH)_2$, magnesium bicarbonate $Mg(HCO_3)_2$ and calcium bicarbonate $Ca(HCO_3)_2$).

Washing and deacidification in the same operation with calcium hydroxide has been studied by Tang (1981)[11]. Shahani et al (1986, 1995)[12, 13] report a decrease in the catalytic action of iron and copper ions in the autoxidation of cellulose after $Mg(HCO_3)_2$ deacidification. Bredereck et al (1990)[14] provide instructions for deacidification in large workshops. Daniel et al (1990)[15] measured enhanced degradation rates for chemical pulp papers deacidified with $Mg(HCO_3)_2$, after exposure to SO_2 and NO_2 pollution. They also found that on the contrary, filter paper and newsprint are protected. Lienardy et al (1990b)[16] studied the washing of paper.

Literature reviews and surveys about deacidification have been authored by Mihram (1986a, 1986b)[17, 18], Lienardy et al (1990b)[19] and Lienardy (1991)[20].

Many scattered reports exist in paper conservation literature concerning the decrease in tensile strength after aqueous treatments. This decrease is usually reported without comments and considered insignificant or irrelevant. As it can be seen from the figures given by Wilson et al (1981, p. 99)[2], after washing or deacidification with magnesium bicarbonate of 14 papers, 12 of them exhibited a decrease in tensile strength. The trend was the same for both washing and deacidification, although it cannot be concluded if the differences between the two treatments are statistically significant since the original data are not available. Lienardy et al (1990b)[16] measured a decrease in tensile strength for a chemical pulp paper and 3 mechanical woodpulp papers after washing in tap water. Green et al (1991)[21] found that Whatman No 2 filter paper suffered a 34-53% loss in tensile strength after washing and aqueous or non-aqueous deacidification. The loss was less for a book paper. Sistach (1996)[8] reports a 30% decrease in tensile strength for the calcium hydroxide deacidified samples and less decrease for the calcium bicarbonate and magnesium bicarbonate deacidified samples. The decrease is attributed mainly to the loss of sizing agents and to the oxidizing action of the alkaline deacidification solution. From the figures given by Adamo et al (1998, p. 45, first row of table 1)[22], it can be seen that washing decreased the tensile strength of Whatman No 1 paper.

In this work, we further investigate the immediate influence of aqueous treatments on the mechanical properties of paper. We are particularly interested in examining if the decrease in tensile strength is due to the removal of size, or it is a more universal phenomenon occurring in unsized paper too. In the latter case, it would manifest some kind of damage to the structure of paper.

2. Experimental

2.1. Specimens

Whatman filter paper no 2 was used in order to test the influence of aqueous treatments on the strength properties of an unsized cellulose paper. Whatman filter paper has been widely used to model pure cellulose paper, since it consists of pure cotton cellulose with no additives, fillers or sizing (Anonymous 2001)[23]. Large quantities of historic paper were also necessary. A part of the historic paper used here has been bought and the rest has been offered from colleges. Six series of samples were finally collected, as can be seen in table 1. The three of them consist of rag paper from the 17th – 18th century, the other two of chemical pulp paper of the 20th century and the last of Whatman no 2 filter paper. Each series of historic paper consisted of the same paper, taken from the same file or booklet. This was verified further by macroscopic observation (identical distances between chain and laid lines, the same watermark, the same color and thickness). The paper used was blank, since writing or printing interferes with the strength properties, as has been observed by Green et al (1991)[21].

Paper Series	Code Name	Fibre composition	Age	Sizing	pH	Thickness (µm)	Grammage (g/m²)
Whatman No 2	W	Cotton	Contemporary	Unsized	7,06	190	103
Historic A	A	Rag	ca. 1650	Gelatin sized	8,60	130	70
Historic B	B	Rag	ca. 1750	Gelatin sized	4,39	240	180
Historic C	C	Rag	ca. 1700	Gelatin sized	6,69	145	68
Historic F	F	Chemical Pulp	ca. 1940	Rosin sized	5,77	110	76
Historic G	G	Chemical Pulp	ca. 1960	Rosin sized	5,41	125	77

Table 1: Description of the samples

2.2. Rationale of the choice of the experimental setup

While working with Whatman paper, we measured significant differences in the mechanical properties among different leaves. This observation verified the inhomogeneity of the same batch of a paper that has been manufactured with high standards and great care. Taking into consideration that handmade historical paper would have been much more inhomogeneous, it was decided that the experimental setup should not be based on the assignment of different treatments to different leaves (or group of leaves). Instead, the paper consisting one series was cut in test-strips (15±0,1 mm wide), which were then randomly assigned to different treatments. This setup safeguarded against the error of attributing existing differences between the different leaves to the different treatments. It also distributed the test-specimens in such a random way that the distributions of the measured values approached normal distributions, fulfilling thus the prerequisite necessary for the application of the t-tests.

2.3. Washing – Deacidification – Consolidation

All the treated specimens were washed with deionized water in the way utilized in a typical archival conservation workshop. The test strips, supported on non-woven polyester fabric (Holytex) were immersed in 3 liters of deionized water (having a conductivity of 0.5 – 1.0 μS/cm and a pH of 5.5 – 5.8) for half an hour. This process was repeated for 2 consecutive times and the paper was drained but not left to dry between treatments. The historic paper of the series A, B, and C was first sprayed with a 70% solution of ethanol in deionized water before the washing, in order to accommodate the fast and homogenous penetration of water.

The third bath was the characteristic of the treatment. The "washed" (H: H_2O) samples were subjected to another identical water bath. The "deacidified" (C: $Ca(OH)_2$) samples were immersed for 0,5 hour in the deacidification bath, which consisted of a semi-saturated calcium hydroxide solution (having a pH of 12,1-12,2) prepared as described by Hey (1979)[24]. The "consolidated" (M: MC) samples were immersed for 0,5 hour in the consolidation bath, consisting of 1% methylcellulose solution in deionized water. Thus, the total immersion time was the same for washed, deacidified and consolidated samples (1,5 hours), enabling thus the comparison of the influence of the different treatments. Reference samples were designated as R. The samples were air-dried without application of pressure in controlled environmental conditions (50 ± 5 % RH, 23 ± 2º C). The use of the supporting fabric was mandatory in order to avoid mechanical damage. Latex gloves were used at every stage for the manipulation of the samples.

2.4. Test Methods

Tensile Strength, Tensile Energy Absorption, Stretch at Break and Folding Endurance were determined according to the appropriate ISO standard (ISO 1924-2 and 5626[25]). The samples were first preconditioned at 23ºC and 25% RH for 24 hours and then conditioned at 23ºC and 50% RH for another 24 hours[26]. Watermarks were not included in the test strips. The number of determinations in each case depended on the quantity of paper, being at least 10 for every mechanical property. All paper series were tested in the cross direction, because more strips were produced and less paper was wasted in this direction.

For the Tensile Properties, a computer-operated instrument made by Zwick was used. The rate of the jaws displacement was 20 mm/min and the initial distance of the jaws was 180 mm. Test strips 21 cm long with a width of 15±0,1 mm were used.

Folding Endurance is equal to the logarithm of the number of double folds. An M.I.T. instrument made by Tinius Olsen, operating at a rate of 175 double folds per minute and a spring tension of 0.5 Kp was used for the determination of the number of double folds. Test strips 15 cm long with a width of 15±0,1 mm were used.

Fourier Transform Infrared Spectroscopy (FTIR) was used for the tracing of gelatin. The FTIR absorbance spectra were collected with the Bio-Rad Excalibur Spectrometer (FTS 3000 MX). The pellets were prepared by scraping with a scalpel the surface of the paper as described by Friese et al (1995)[27], drying for 48 hours at 48 ºC and 0,5 atm pressure 7 mg of the scrapings, mixing them with 100 mg of dry KBr and pressing it at a pressure of 8 – 9 tn for 2,5 minutes.

The cold-extraction pH was determined according to ISO 6588[28]. Twice distilled water (Merck) was used, having a conductivity of 0,60 µS/cm. The value reported in table 1 is the average of two determinations.

The sorption – desorption isotherm at 23ºC was recorded by an automatic analyzer (CI SORP analyzer) made by CI Electronics Ltd. The water content of the sample is recorded gravimetrically as the relative humidity in the sample chamber changes in steps of 10% (Anonymous[29], Mangel 1999[30]).

3. Results

3.1. F.T.I.R. Spectroscopy

FTIR results positively indicate the use of a proteinaceous material (gelatin) as size in papers A, B and C. In figure 1, the infrared absorption spectra of paper B before and after deacidification and Whatman No 2 paper can be seen. The absorption bands at 1652 cm^{-1} (attributed to C=O stretching of mono-substituted amides) and 1538 (attributed to C – N – H bending of mono-substituted amides) that appear in the spectrum of paper B and are absent from the spectrum of Whatman paper are characteristic of monosubstituted amides and indicate the presence of a protein (Pavia et al 1996, Choisy et al 1997, Proniewicz et al 2001, Waterhouse et al 1991, Barrett et al 1996) [31, 32, 33, 34, 35]. It has been well established that animal glue (a crude form of gelatin) has been used for the sizing of paper contemporary to the samples A, B and C (Hunter 1974, Barrett 1989, Barrett et al 1996) [36, 37, 35]. Since the intensity of the gelatin characteristic peaks diminished after aqueous treatments for these 3 papers, a part of it must have been solubilized and removed by water.
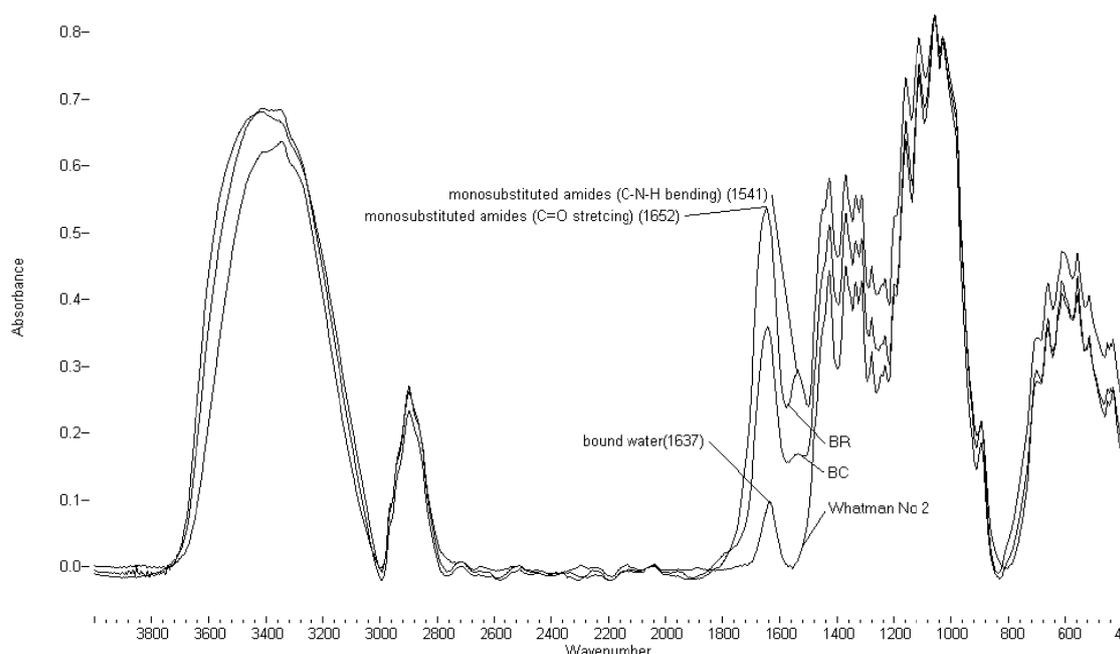
Fig. 1. FTIR spectra of paper BR (reference – upper trace), BC (deacidified – middle trace) and Whatman filter paper No 2 (lower trace). All the spectra have been baseline corrected.

3.2. Mechanical Properties

The influence of deacidification on the strength properties of the samples is shown in Fig. 2, 3, 4 and 5.

Folding Endurance	W	A	B	C	F	G
R	1.34	2.79	1.80	2.31	1.30	1.23
C	1.27	2.64	1.92	1.90	1.32	1.29
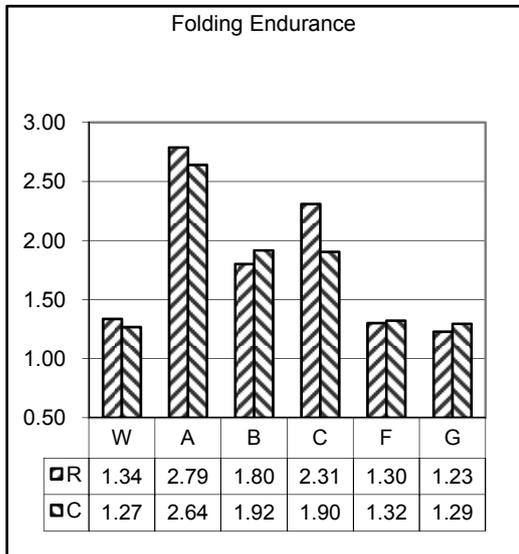
Fig. 2: Folding Endurance of Reference (R) and deacidified samples (C)

Tensile Strength (N/m)	W	A	B	C	F	G
R	1799	1842	4642	1834	1050	1104
C	1580	1706	3567	1491	992	1082
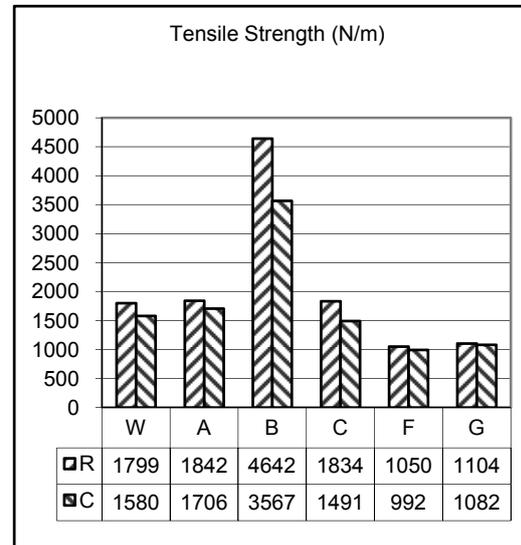
Fig. 3: Tensile strength of Reference (R) and deacidified samples (C)

Tensile Energy Absorption (N/m2)	W	A	B	C	F	G
R	39	62	134	58	20	18
C	44	57	104	46	25	26
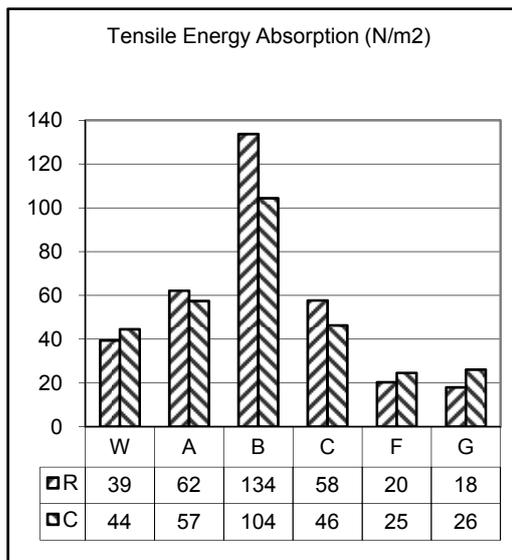
Fig. 4: Tensile Energy Absorption of Reference (R) and deacidified samples (C)

Stretch at Break ΔL%	W	A	B	C	F	G
R	2.73	4.43	3.75	4.09	2.43	2.13
C	3.62	4.64	3.86	4.20	3.00	3.04
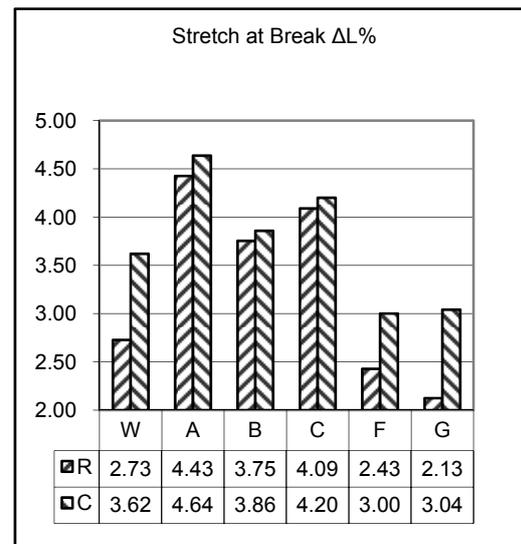
Fig. 5: Stretch at Break of Reference (R) and deacidified samples (C)

The results of washing, deacidification and consolidation on Folding Endurance and Tensile Strength of Whatman paper and historic paper A are shown in Fig.6 and 7.
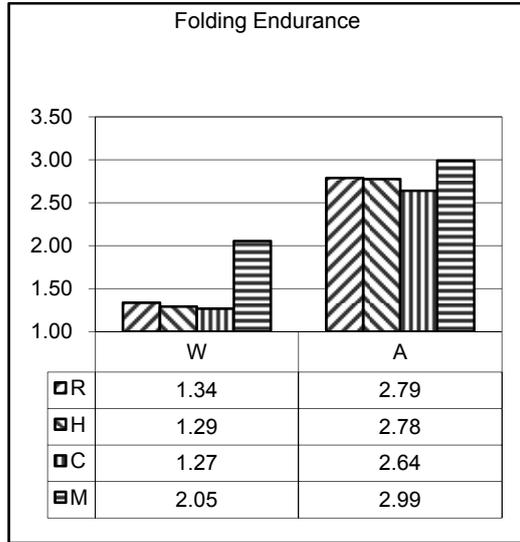
Fig. 6: Folding Endurance of Reference (R), Washed (H), Deacidified (C) and Consolidated (M) samples of Whatman and paper series A.
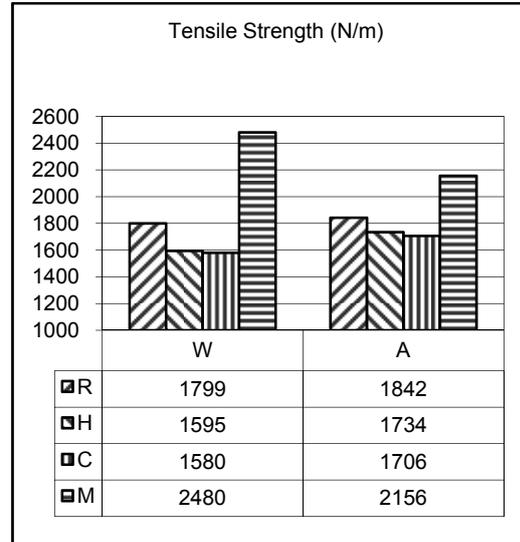
Fig. 7: Tensile Strength of Reference (R), Washed (H), Deacidified (C) and Consolidated (M) samples of Whatman and paper series A.

The mean values, the standard deviations and the number of determinations for all mechanical tests are shown in table 2.

Sample Code	FE			TS (N/m)			SAB (ΔL %)			TEA (N/m2)		
	Mean	Stdev	Det.	Mean	Stdev	Det.	Mean	Stdev	Det.	Mean	Stdev	Det.
WR	1,34	0,08	20	1799	66	12	2,73	0,18	12	39,4	4,0	12
WH	1,29	0,08	20	1595	55	12	3,57	0,40	12	44,6	7,2	12
WC	1,27	0,07	20	1580	66	12	3,62	0,37	12	44,5	6,4	12
WM	2,05	0,28	17	2480	129	12	4,38	0,55	12	84,0	15,0	12
AR	2,79	0,26	17	1842	161	13	4,43	0,58	13	62,1	12,5	13
AH	2,78	0,22	16	1734	229	12	5,12	0,62	12	66,1	16,9	12
AC	2,64	0,22	18	1706	137	12	4,64	0,61	12	57,4	12,3	12
AM	2,99	0,17	10	2156	157	12	4,98	0,50	12	80,3	12,2	12
BR	1,80	0,17	20	4642	827	13	3,75	0,82	13	133,7	52,4	13
BC	1,92	0,18	20	3567	502	12	3,86	0,86	12	104,4	37,1	12
CR	2,31	0,18	10	1834	209	11	4,09	0,72	10	57,7	15,7	10
CC	1,90	0,21	10	1491	167	13	4,20	0,58	13	46,2	10,3	13
FR	1,30	0,14	19	1050	29	11	2,43	0,40	11	20,3	4,0	11
FC	1,32	0,11	16	992	51	11	3,00	0,43	9	24,5	4,4	9
GR	1,23	0,14	16	1104	25	12	2,13	0,42	12	18,0	4,4	12
GC	1,29	0,13	16	1082	35	11	3,04	0,52	11	26,0	5,6	11

Table 2: The mean values (Mean), the standard deviations (Stdev) and the number of determinations (Det) for all mechanical tests.

3.3. Statistical Elaboration of the Test Results

The student t test (supposing non-equal variances, at 95% confidence level) was used for the comparison of the mean values of the mechanical properties before and after the deacidification treatment. This test indicates if the differences between the mean values are statistically significant or they can be attributed to random variations. The null hypothesis is always that mean1=mean2 and the alternative hypothesis that mean1>mean2, or mean1<mean2, i.e. that the mean value decreased or increased respectively. The results are presented in table 3.

	W	A	B	C	F	G
Folding Endurance	⇓	⇓	⇑	⇓	↑	↑
Tensile Strength	⇓	⇓	⇓	⇓	⇓	↓
Stretch at Break	⇑	↑	↑	↑	⇑	⇑
Tensile Energy Absorption	⇑	↓	↓	⇓	⇑	⇑

Table 3: Changes induced by deacidification to the mechanical properties of the samples. ⇓⇑ : Significant at 95% confidence level. ↓↑: Insignificant at 95% confidence level.

4. Discussion

It is generally believed that the most important mechanical property, as far as the conservation scientist is concerned, is folding endurance, since an increase in folding endurance would increase the pliability of the paper, making it more usable. Furthermore, folding endurance is very sensitive to accelerated ageing whereas tensile strength is not. Tensile Energy Absorption is also thought to be important, since an increase in TEA indicates that paper can absorb more energy before it fails (Wilson et al 1981)[2]. Another favorable mechanical property is Tearing Resistance. Barrow et al (1959)[38] postulate, "Because it was found that 3 out of 4 of the total (books) sample tested … were constructed with the machine direction of the paper parallel to the spine, it appeared that the significant tests for measuring the resistance of paper to the strains imposed upon it in the natural use of books are those for folding endurance in the cross direction and for tear resistance in the machine direction". These three mechanical properties are mostly used for the evaluation of conservation treatments on paper. Tensile strength is not considered a suitable criterion for such an evaluation (Wilson et al 1981 p. 99[2], Brandis 1994[39]) because a brittle (thus unusable) paper can exhibit a high value of tensile strength (Bansa et al 1997[40]).

Nonetheless, the paper of a historic document or a page of a book are not expected to bear tensile loads, or folded back and forth while pulled at the same time. In material testing, mechanical strength properties are examined for the determination of the ability of a material to bear loads, but also because they reflect the impact of different treatments on chemical and physical properties and structure. It is this connection to chemical, physical and structural properties that primarily motivates paper conservation scientists to perform strength tests. From this point of view, all strength tests are important, especially if they can register alterations caused by different treatments.

In this work, 5 out of 6 of the treated samples exhibit a statistically significant decrease in tensile strength (fig. 3 and table 3). As it can be seen in fig. 7, the decrease in tensile strength results from either washing or deacidification (student t test indicates that differences between H and C samples are insignificant). This observation leads to the conclusion that the aqueous treatments are responsible for the decrease in tensile strength. Our results are in accordance with the reports discussed in the introduction; nevertheless, we believe that the implications of them have to be reconsidered.

Initially, the hypothesis that the loss of tensile strength of treated paper could be attributed to the plastisizing effects of excess moisture had to be checked. It is well known[41] (Salmen et al, 1980) that an increase in the moisture content results in a decrease in tensile strength. Aqueous treated paper could retain an excess of water after air-drying when compared to the untreated, even after preconditioning. Strips of Whatman filter paper, reference (R) and treated (H, C, M) were dried in an oven at 105ºC and reduced pressure (0,5 atm) for 4 hours. After this treatment, all water has been removed. The strips were then preconditioned, conditioned and tested for tensile strength as described above. The results left no doubt. Even after

drying, the aqueous-treated samples exhibited a statistically significant decrease in tensile strength (fig. 8). From these results, it can also be concluded that preconditioning can satisfactorily bring the moisture content of the treated paper to levels that do not affect tensile strength.

Tensile Strength (N/m) - Whatman MD

	Not Dried	Dried
R	2565	2662
H	2237	2155
C	2158	2276
M	3242	3282
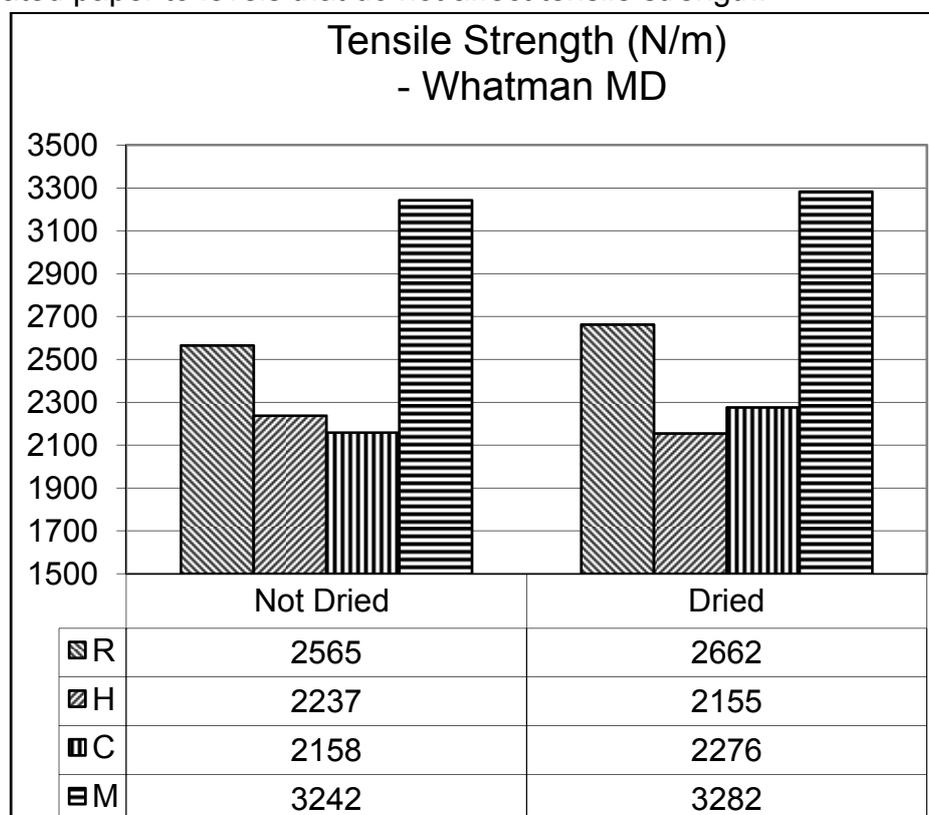
Fig. 8: Tensile Strength of not dried and dried samples of Whatman paper
(Machine Direction, 10 strips each category)

The decrease of tensile strength of the historic samples after aqueous treatments could be attributed to size removal. This decrease though, is observed for the Whatman paper as well, which is not sized, and reported in the literature for quite different kinds of paper. Thus, the decrease in tensile strength must be a universal phenomenon, attributed to an intrinsic damage of paper. Whether this damage is of chemical or mechanical nature or both cannot be answered without further research, but using the existing evidence we think that chemical damage must be small, if any. There are no reports in the literature that washing in deionized water has an impact on the degree of polymerization of cellulose. Since tensile strength depends on the strength of the fibers and on bonding, if fiber damage is excluded, it can than be concluded that bonding is negatively affected by immersion in water and subsequent drying. Nevertheless, cellulose could be chemically damaged at the wet – dry interface, as the wet boundary advances, due to mechanical stresses arising from humidity changes, which could cause chain cleavage (Pedersoli 2001)[42]. Another plausible explanation, favoring the mechanical damage hypothesis, could be the following: The wetting and drying of paper does not occur instantaneously and homogenously; as the dryer areas lag behind in swelling, cellulose fibers are pulled out of the more wet matrix, which swells at a faster rate. Both processes described above could take place when a droplet of water wets a small spot of a paper leaf: After drying and if the paper is weak enough, the spot becomes loose and can be

detached by pressing with a finger. This example is a fact that conservators must bear in mind when applying local aqueous treatments.

Furthermore, the measurements of the other mechanical properties collected in this work tend to support the fact that wet processes could impair the strength of paper, regardless of what the cause is. According to our measurements, folding endurance decreases in 3 out of 6 cases (fig. 2); for the three of them the decrease and for the one of them the increase are statistically significant (table 3). Tensile Energy Absorption decreases in 3 out of 6 cases (fig. 4), the decrease being significant in one case as is the increase in three others (table 3). The increase in TEA is due to the increase of stretch at break (fig. 5). An extensive survey in the relevant literature indicates that the mechanical behavior of aqueous treated paper is far from uniform. Most of the researchers report a definite increase in folding endurance (see for instance Sclawy 1981[43], Lienardy 1990a[16]) and tensile energy absorption. Increase in folding endurance has been reported by us previously[44]. There are many scientists, though, reporting mixed trends, seemingly depending on the kind of paper (Wilson et al 1981[2], Bansa 1992[45], Bansa 1997, see the first two columns of tables 2 and 3, page 59-60[40], Bansa 1998, see page 20, table 6 and page 23, table 7a [46]), not only as a result of aqueous but of non-aqueous deacidification as well (Porck 1996)[47].

A word of caution should be added here, concerning the testing of folding endurance. Folding endurance measurements are very sensitive to the moisture content of paper. A small increase in moisture content can cause a considerable increase to this strength property (Sclawy 1981[43]). The moisture content of paper depends primarily on environmental relative humidity (R.H.) and less on temperature. That is why, conditioning to standard atmosphere (23º C and 50% RH) for at least 24 hours is necessary before testing. However, the direction from which the 50% R.H. is approached plays an important role. If environmental humidity approaches 50% from a lower R.H., the paper sample contains less water than if 50% R.H. is approached from a higher R.H. This phenomenon, called hysteresis effect (see fig. 9), is very well known to paper industry. TAPPI standard for conditioning (TAPPI T 402[26]) requires a preconditioning step of 24 hours to lower R.H. (20-35%), so that moisture content of paper is univocally defined. This preconditioning step is imperative when comparison of folding endurance before and after aqueous treatments is attempted. If it is omitted, the washed papers, which approach 50% R.H. from 100% R.H. will contain more water at the equilibrium than if they were preconditioned, giving thus higher values of folding endurance. Surveying the relevant literature, we noticed that although conditioning before testing is always mentioned, preconditioning is rarely done so (see for example Shahani et al 1984 p. 391[12], Tang 1984 p. 429[48]). The lack of preconditioning could explain why decrease of folding endurance after aqueous treatments is rarely reported.
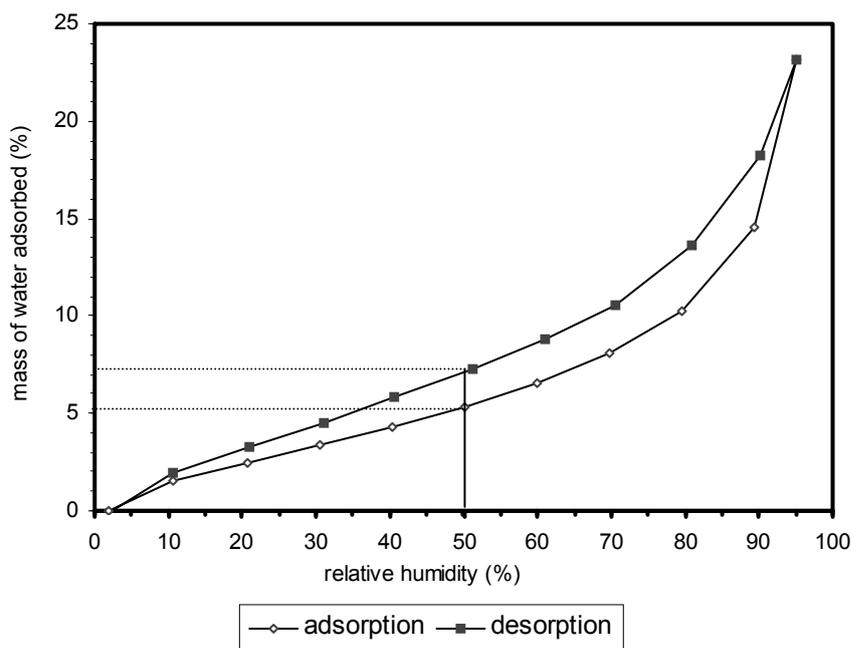
Fig. 9: Hysteresis effect in moisture sorption of Whatman filter paper. If 50% R.H. is approached from below (adsorption), the moisture content of paper is about 5%. If 50% R.H. is approached from above (desorption), the moisture content of paper is about 7%. The graph has been recorded at 23°C by CI Sorp Analyzer.

Even if the decrease in the mechanical strength is not the rule, and even if no damage is inflicted to paper but the weakening is simply because of the removal of size, there are still some important implications to be considered:

- The tenet that any paper (with stable inks or colors in water) would benefit from washing is very common in the relevant literature (see for example: Hey 1979[1], Dupont 1996[49]), but it appears that it is not always justified. We believe that caution should be exercised and according to the principle of minimum intervention, washing and deacidification should be applied only to acidic paper. Strong, neutral or alkaline paper should not be washed or deacidified, at least as a principle, if there are not other reasons dictating such interventions.

- If for some reasons (i.e. heavily stained or/and acidic paper) the decision to proceed to aqueous treatments is taken, consolidation of the paper should be implemented, so that the initial strength is restored or even surpassed. This is particularly important when local aqueous treatments are applied on weak paper. As can be seen in fig. 6 and 7 and is reported in the literature, application of methylcellulose or gelatin solutions has the desired result. Methylcellulose has been proved not to influence negatively the ageing of paper (Strnadova et al 1994[50]). The very good condition and mechanical properties of papers A and C is the best proof that gelatin does not harm paper either. Indeed, according to many researchers, it appears that gelatin is highly beneficial (Barrett 1989[37]. Wet pressing, whenever can be applied, could also restore some of the lost strength.

- Chemical stabilization versus mechanical weakening: It has been well established that deacidification increases the useful life of paper

documents, since it retards their ageing. If strength is unaffected or increased after treatment, this concept is correct (fig. 10a). However, if the strength of paper decreases after treatment, the above statement could be false. As one can see in fig. 10b, although treated paper ages better, the properties of the untreated paper are always better than the properties of the treated one. If the lines meet, as in fig. 10c and 10d, then the position of the intersection is important. If the intersection point lies close to the present (say, within 20 years from today, fig. 10c), then the properties will be enhanced for the most part of the life of the document. This could happen when a highly acidic paper is deacidified; even if there is an initial strength loss, the slope of the strength decrease due to ageing would be much steeper for the non-deacidified paper than for the deacidified one. If though the intersection point lies far in the future, until that time is reached, users will be manipulating an object with reduced strength, inflicting more damage to it and practically accelerating its ageing (not linearly but in a rather accelerating stepwise manner). The result of this process could be that the intersection point would move further towards the future or cease to exist, since the two lines would never intercept (fig. 10d). Cases 10b and 10d could describe the performance of a neutral or alkaline paper, when there is no significant improvement of the ageing rate. These scenarios are purely fictitious and simplified (the lines are drawn straight for simplicity), but make very clear the point that if there is a decrease in the strength of paper, there is much uncertainty if the results of the intervention are beneficial or harmful.

Unfortunately, since only destructive reliable tests exist for the measurement of the strength of paper, there is no way that a conservator would know the results of the treatments applied to any specific paper. The above-mentioned precautions will hopefully guard against this uncertainty.
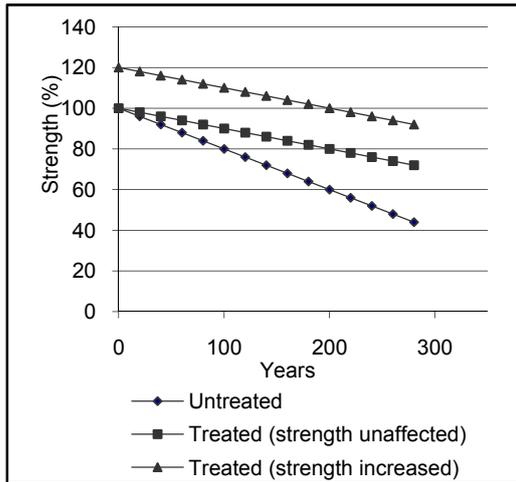
Fig. 10a: Beneficial treatment. Initial strength after deacidification is unaffected or increased.
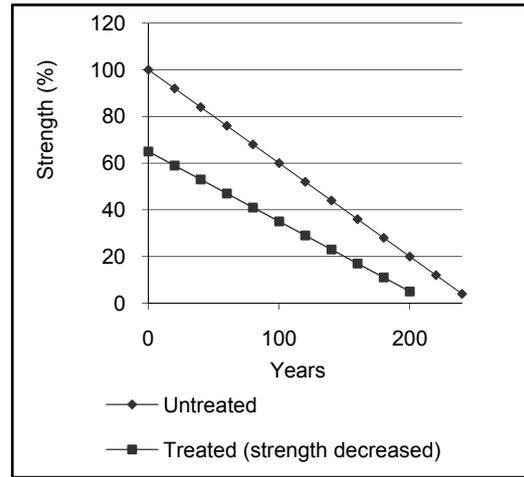
Fig. 10b: Initial strength decreases due to deacidification. There is a case, as depicted above, that even if the treated paper ages better, the untreated has always higher strength.
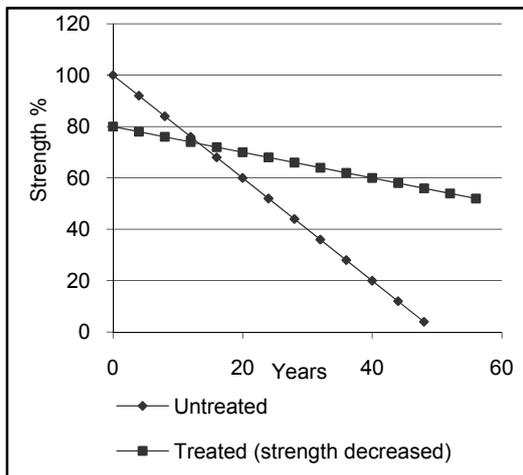
Fig. 10c: The intersection point lies close to the present. Although there is a decrease in the initial strength due to deacidification, the properties of treated paper are better for the most time of its life.
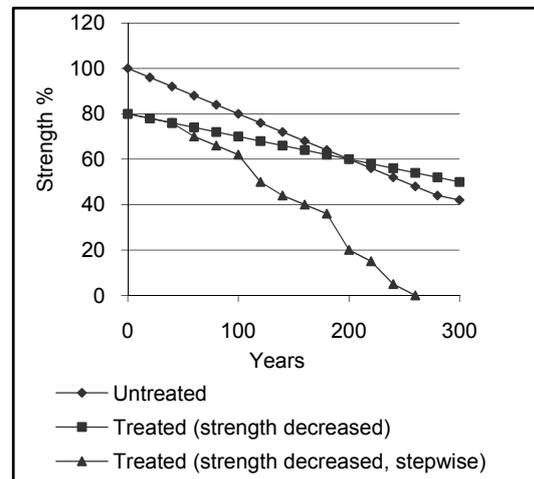
Fig. 10d: The intersection point lies far in the future. Until that time is reached, more damage will be inflicted to the weakened paper. The paper will not follow the straight line but will deviate from it in a stepwise manner towards lower strength.

Fig. 10: Hypothetical scenarios showing different impacts of deacidification on the strength properties of paper. The lines are drawn straight for simplicity and do not reflect a specific model of degradation kinetics.

5. Conclusions

Based on our research and literature, we postulate that aqueous treatments could, at least in some cases decrease the strength of paper, especially tensile strength. It is well known that tensile test is insensitive to accelerated ageing. It is very sensitive though to changes due to aqueous treatments as it can register either removal of size or/and structural damage of paper. Therefore, we consider tensile strength testing equally important to folding endurance, tensile energy absorption and tearing resistance tests, especially for the evaluation of the immediate impact of washing and aqueous and non aqueous deacidification. We also think that mechanical strength tests are indispensable, since there are changes after aqueous treatments that cannot be detected by chemical tests like the determination of the degree of polymerization of cellulose. We propose that aqueous treatments should be applied only when necessary (i.e. acidic paper) and that they should be followed by consolidation.

Preconditioning before testing is also considered imperative when mechanical properties and especially folding endurance are compared before and after aqueous treatments.

Finally, the remarkable folding endurance values of papers A and C must be emphasized. Although these two papers are at least 300 years old, they are still in perfect condition, a confirmation that good raw material (cotton rags), patient processing and gelatin sizing can do miracles.

We believe that research has to be directed on developing criteria for the prediction of the response of the strength properties of paper after aqueous treatments. Paper B for instance, whose folding endurance definitely increased after deacidification, was highly acidic and significantly thicker than the other papers. The need for non-destructive strength tests was also made clear in this study, since such a test would resolve the uncertainty of the outcome of an aqueous treatment on any paper object.

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