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Effect of Water Washing on Paper and Cellulosic Textiles: An Overview and Update of CCI Research

ABSTRACT

Between 1986 and 1995, eight studies using old, new, and chemically treated papers and textiles were conducted at the Canadian Conservation Institute (CCI). In total, forty-two papers and nine cellulosic textiles were studied to address the effect of deionized water washing; the benefits and dangers of washing with magnesium bicarbonate and sulfate solutions; the uptake of cations by paper; and the effectiveness of washing solutions in removing acids from papers. This paper summarizes these data, provides an overall picture on the impact of these treatments on paper and cellulosic textiles, and answers some of the questions relating to deionized water washing and alkaline sensitivity.

1. INTRODUCTION

Water washing is one of the most useful cleaning treatments for paper and textile conservators. Where an artifact can be safely wet-cleaned, water washing can often improve the appearance more than any non-aqueous cleaning method. The process can also improve the long-term stability of an artifact by removing water-soluble pollutants and harmful degradation products.

As water washing is widely used, it is important for paper and textile conservators to understand its impact on artifacts. One of the greatest concerns is the choice of water quality. At the root of this is the fact that deionized (DI) water is 'aggressive.' Research has shown that washing with deionized water can remove calcium and magnesium ions from cellulose and can lead to weakening of the fibers over time (Tang and Jones 1979). The second concern is the effect of alkali on highly oxidized cellulose such as very old or over-bleached paper, cotton, and linen (Golova and Nosova 1973; Kolar and Novak 1996). Although addition of deacidification chemicals to wash water has been shown to slow down the rate of deterioration of paper (Tang 1981), the possibility of alkaline degradation (often referred as 'alkaline sensitivity') needed to be addressed. These concerns together with reports of magnesium bicarbonate causing fading of iron-gall ink (Hey 1981–82) and yellowing of papers, commonly associated with cellulose degradation (Calvini, et al. 1988), have caused many conservators to refrain from deacidifying paper artifacts that might have otherwise benefited from it. It was necessary to establish whether alkaline sensitivity occurs in the conditions (type of deacidification chemical, concentrations, pH, temperature, and duration) used for conservation treatment.

Between 1986 and 1995, eight studies using old, new, and chemically treated papers and textiles were conducted at the Canadian Conservation Institute (CCI). In total, forty-two papers and nine cellulosic textiles were studied to address the effect of deionized water washing; the benefits and dangers of washing with magnesium bicarbonate and sulfate solutions; the uptake of cations by paper; and the effectiveness of washing solutions in removing acids from papers. This paper summarizes these data, provides an overall picture on the impact of these treatments on paper and cellulosic textiles, and answers some of the questions relating to deionized water washing and alkaline sensitivity. Details from these studies are being compiled (Tse 2001).

2. SUMMARY OF THE EIGHT STUDIES

The DI water used in these experiments was purified by reverse osmosis (RO) or distillation followed by deionization, organic removal, and submicron filtration. The water had specific resistance of 18 MS-cm. In most of the studies magnesium (Mg) salts were used for treatment. Magnesium and not calcium (Ca) salts were chosen because of their solubility, which allowed treatment at

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higher solution concentrations. Cellulose literature also suggested that magnesium is able to stabilize cellulose during oxidation. Degradation of cellulose was measured by a number of techniques, but the degree of polymerization (DP) was preferred because of its sensitivity and precision. 'Stability' of a sample, as a result of treatment, is referred to the percentage of change, usually DP, before and after thermal aging at a single aging interval. The greater the decrease in DP, for example, the less stable the sample.

Study #1 Effect of water washing on the stability of a very old cotton textile—1986 (Burgess 1986)

This experiment was designed to verify the destabilizing effect of DI water and the benefits of adding low concentrations of calcium salts to the wash water. An eight hundred-year-old cotton textile was washed by immersion in tap water, DI water, 20 mg/L of calcium sulfate ($CaSO_4$), and 20 mg/L of calcium bicarbonate ($Ca(HCO_3)_2$). The treated cotton and untreated control were aged at 70°C, 50% RH for 10 weeks. Degradation of the cotton was measured by gel permeation chromatography (GPC) and DP.

Both GPC and DP results showed that tap water and calcium sulfate increased stability of cotton during aging, but distilled/deionized water and calcium bicarbonate decreased its stability. This was interpreted as evidence of destabilization of cellulose by DI water washing and sensitivity of very old (presumably oxidized) cotton to alkali. Therefore it was necessary to study the effect of these treatments on old papers and to assess their susceptibility to alkaline sensitivity.

Study #2 Effect of alkali on rag and processed wood papers—1988 (Burgess, Duffy, and Tse 1991; Burgess, Duffy, and Tse 1990–91)

Eleven 'old' lignin-free (rag and processed wood pulp) book and ledger papers were used in this study. These were washed in DI water, 20 and 200 mg/L of Mg in magnesium bicarbonate ($Mg(HCO_3)_2$), and 20 and 200 mg/L of Mg in magnesium sulfate ($MgSO_4$).The treated papers and the untreated controls were aged at 70°C, 50% RH for 8–12 weeks. Degradation of the papers was measured by DP, pH, and scanning electron microscopy/energy-dispersive X-ray (SEM-EDX) microanalyses for Ca and Mg.

The calcium and magnesium content of all the papers decreased with DI water washing, but not all the papers became less stable as measured by DP. DI water washing caused some papers to be more stable, some less stable during thermal aging. There was no *consistent* evidence showing that papers were destabilized by DI water washing. Among the samples treated in magnesium solutions, all the papers became more stable with increased pH. Low concentration (20 mg/L) of magnesium sulfate was found to improve the stability of most papers.

Study #3 Effect of alkali on lignin-containing hand sheets—1990 (Duffy 1990)

Since there was no evidence of alkaline sensitivity at 200mg/L bicarbonate treatment used in Study #2, the concentration of the solutions was increased to include 2000mg/L of Mg, and a small amount of lignin was introduced into the test papers to see if lignin-containing papers were more susceptible to alkali degradation.

Four sets of handsheets composed of 0:100, 25:75, 50:50, and 100:0 flax%:unbleached kraft pulp% (~5% lignin) were prepared. These were washed in DI water; 20, 200, 2000 mg/L of Mg in $Mg(HCO_3)_2$ and 20, 200, 2000 mg/L of Mg in $MgSO_4$; and aged at 80°C, 50% RH for 8–11 weeks. Degradation of the papers was measured by DP, zero-span tensile strength, alkaline reserve, pH, color, and SEM-EDX microanalysis for Ca, Mg, S, Na, K.

All the bicarbonate-treated handsheets became more stable during aging, and the benefits increased with increased concentration of bicarbonate. Yellowing or darkening of the sheets, especially with higher percent of kraft pulp, was observed, but this did not correspond to a decrease in stability as measured by DP (the amount of lignin in the handsheets was not large enough to interfere with DP analyses). This was an indication that yellowing or darkening of lignin-containing sheets may not mean degradation. The sheets treated by 2000 mg/L $MgSO_4$ showed a substantial decrease in stability even though the sheets had a neutral pH. There was a poor correlation between stability and magnesium (Mg) or calcium (Ca) content, but there was a good correlation between stability and pH.

Study #4 Uptake of magnesium and calcium in papers—1992 (Burgess and Boronyak-Szaplonczay 1992).

The purpose of this study was to compare the absorption behavior of different types of papers, including those that were oxidized and lignin-containing. Seven papers (rag, wood pulp, lignin-containing, and artificially oxidized with hypochlorite) were immersed in increasing concentrations of calcium and magnesium salt solutions: 20-2000 mg/L of Mg in $Mg(HCO_3)_2$ and $MgSO_4$; 20-900 mg/L of Ca in calcium hydroxide ($Ca(OH)_2$); 20-300 mg/L of Ca in $Ca(HCO_3)_2$. The calcium and magnesium cation uptake by the treated papers was determined by flame atomic absorption analyses (FAA). The papers were not artificially aged.

The results showed that calcium and magnesium cation uptake increased with solution concentration and did not reach a 'plateau' as many believed. Calcium hydroxide-treated papers had much higher uptake than the bicarbonate-treated papers. Sulfate-treated papers had the lowest uptake. It was clear that the pH of solution was the determining factor for cation uptake. The influence of the anion, whether it was sulfate or bicarbonate, was comparatively small. Lignin-containing and hypochlorite-bleached papers were also found to absorb slightly more calcium and magnesium than lignin-free and unoxidized papers.

Study #5 Effect of alkali on the lignin-containing papers—1992 (Burgess and Goltz 1994)

In study #3, the yellowing of the handsheets after treatment in 200 and 2000mg/L of magnesium bicarbonate needed further investigation. In this study, eight lignin-containing papers were used to look for possible evidence of alkaline sensitivity.

Eight lignin-containing papers and one alkaline cotton commercially made paper were immersed in DI water; 20 mg/L of Mg in $MgSO_4$; 20, 200, and 2000 mg/L of Mg in $Mg(HCO_3)_2$. The treated and untreated controls were aged at 80°C, 50% RH for 4 weeks. Degradation of the papers was measured by DP, zero-span tensile strength, alkaline reserve, pH, color, and FAA for Mg.

At the time of this study, the DP technique was not very reliable for analyzing lignin-containing papers, so zero-span tensile strength data were also used to substantiate the DP results. Based on the DP and zero-span tensile strength results, six out of the eight lignin-containing papers became more stable after treatment with bicarbonate solutions. In most cases, the benefit increased with bicarbonate solution concentrations. The bicarbonate-treated papers yellowed, but did not correspond to lower DP or zero-span tensile strength. There were varying degrees of loss in magnesium from the papers as a result of DI water washing, but there was no consistent evidence of destabilization.

Study #6 Effect of alkali on peroxide-bleached pulp and paper—1993 (data unpublished)

The purpose of this study was to look for evidence of alkaline sensitivity by using artificially oxidized paper and pulp. Flax pulp and a rag book paper (c. 1734) were oxidized in 2% hydrogen peroxide (pH 9 and 10), prior to washing in DI water; 20, 200, and 2000 mg/L of Mg in $Mg(HCO_3)_2$; 20, 200, and 2000 mg/L of Mg in $MgSO_4$. They were aged at 80°C, 50% RH for 11 weeks. Degradation of the pulps and papers was measured by DP, carbonyl content, and color measurements.

The results revealed more about the stabilizing effect of peroxide bleaching, and the effectiveness of the various stabilizers than alkaline sensitivity. Neither the peroxide-bleached pulp nor the rag paper showed any evidence of alkaline sensitivity after treatment in 2000 mg/L of magnesium bicarbonate. They benefited from it. The destabilization of the flax pulp after treatment in 200 and 2000mg/L of magnesium sulfate, observed in study #3, was again confirmed.

Study # 7 Removal of acids from paper by washing—1994 (Woods 1994)

At this point, there was no consistent evidence of the destabilizing effect of DI water washing on paper, but the benefits were also not consistent. The effect varied from paper to paper, and it depended on the quantity of acid originally present and its solubility in water. It was also clear that the benefits of alkalization outweighed the potential danger with most of the test materials. It was important to know the rate and the amount of acid removal from different papers by DI water washing and the benefits of adding small amounts of calcium and magnesium salts.

Six different old papers, both rag and wood pulp, were washed in DI water for up to 120 minutes. One of the six papers, an acidic lignin-containing paper, was also washed with 20 mg/L of $MgSO_4$, $Mg(HCO_3)_2$, and $Ca(OH)_2$ for up to 60 minutes. Papers were removed from the washing bath at different intervals. The analyses used were iodometric total acid, pH, and FAA (for Mg, Ca, Fe, Na, K).

The quantity of acids in the papers varied; the proportion of acids removed by washing also varied from paper to paper. DI water alone removed between 5–40% of the total acids within the first 10–20 minutes. With the acidic lignin-containing paper, addition of 20 mg/L of $Mg(HCO_3)_2$ and $Ca(OH)_2$ increased acid removal from 40% up to 70%.

Study # 8 Effect of washing on cotton and linen textiles—1995 (data unpublished)

The last of these eight studies looked at the effects of washing on textiles as compared to papers.

Eight cotton and linen textiles, with a range from high to low DPs, were used. They were washed in DI water, 20 mg/L of Mg in $Mg(HCO_3)_2$ and $MgSO_4$. The washed textiles and controls were aged at 80°C, 50% RH for 8 weeks. The cation content (Ca, Mg, Na, K, Fe) of the textiles before and after washing was measured using FAA, and the degradation before and after aging was measured by DP.

DI water washing did cause a decrease in calcium and magnesium content in the textiles, but there was no obvious positive or negative effects as measured by DP. The differences in DP between treatments, for most of the textiles, were very small. The benefits from bicarbonate and sulfate treatments were also much less obvious compared to paper. This suggested that in order for textiles to benefit from the treatment, higher concentrations of neutral or alkaline salt solutions may be required.

3. CONCLUSIONS

These eight studies were not without flaws and the results not without ambiguity. For instance, in six out of the eight studies, DP was used as the main indicator of cellulose degradation. While DP is an excellent indicator, the technique is limited in that it only measures molecular chain length of what was left behind in the paper and textile after washing. What was removed during washing was not accounted for. While the results are related to the strength of the paper, DP does not give information about other changes in mechanical properties of the paper after treatment, changes that may result from the loss of sizes and fillers and interruptions to interfiber bonding.

Despite the ambiguity of some of the results, the shortcomings of some experimental designs, and the limitations of the analytical techniques, there are definite patterns in the data.

Is it safe to use DI water for washing?

The results from our studies showed that the main shortcoming of washing in DI water is not destabilization of cellulose through the loss of calcium or magnesium ions, but its ineffectiveness in removing acids. DI water washing did result in a decrease in the calcium and magnesium content in most papers and textiles, but there was no consistent evidence that this *caused* paper or textiles to be chemically less stable during artificial thermal aging. On the other hand, there was a much stronger correlation between the pH and chemical stability of papers and textiles. Results also showed that DI water was able to remove some of the acids in paper, but addition of even a small quantity of magnesium or calcium salts greatly enhanced the benefits of washing by partial neutralization and by ion exchange, especially with addition of calcium hydroxide.

Was there any evidence of alkaline sensitivity with the use of high concentrations of magnesium bicarbonate?

Since the overall results showed that *acidity,* and not the loss of calcium (Ca) or magnesium (Mg) ions, was the *main cause* for cellulose destabilization during aging, deacidific ation would be the most important preventive treatment for paper and cellulosic textiles. Any possible damage from deacidification, such as alkaline sensitivity, would be important to know in determining treatment strategies.

Our results showed that magnesium bicarbonate stabilized most papers during thermal aging, but it caused yellowing and darkening in lignin-containing papers. At low concentrations, the benefits on paper were much more evident than that observed in textiles. Magnesium sulfate stabilized papers at low concentrations (20 mg/L), possibly by more effective removal of acids in paper via ion exchange. But at higher concentrations it appeared to destabilize some papers (e.g. flax pulp) significantly. There was no convincing evidence of alkaline sensitivity with most naturally aged (and peroxide-bleached) rag or processed wood-pulp and lignin-containing papers. These results did not eliminate the possibility of alkaline sensitivity for very old or severely oxidized papers or textiles such as the eight hundred-year-old cotton used in the study #1. However, it was clear that, in most cases, the benefits of deacidification greatly outweighed the risk of damage, and it is crucial to deacidify acidic papers and textiles, whether by ion-exchange and/or neutralization.

4. GUIDELINES FOR WASHING

Based on our results and those from other research (Tang 1981; Bogaard 2001), the following guidelines are recommended:

pH 6-7

For materials that are potentially sensitive to alkali (e.g. alkali-sensitive colorants; very weak or over-bleached papers or textiles), neutral (pH 6–7) treatment solutions should be used. Washing with neutral calcium or magnesium salt solutions will increase the removal of extractable acids. Our results suggested that magnesium sulfate solutions should only be used at low concentrations (20 mg/L). Immersion in calcium salt solutions followed by DI water rinse have been shown to be very effective in removing acids from oxidized paper without causing damage, and in turn protecting these papers during artificial thermal aging (Bogaard 2001).

pH 8.0-8.5

For materials that can tolerate up to pH 8–8.5 (e.g. some iron-gall ink corroded papers; old but fairly robust papers or textiles), using diluted calcium hydroxide (or alkaline water) is probably the most effective way of washing. It is much more effective in removing acids than DI water wash. It also adds a small quantity of calcium to the paper. A 1–2:1000 dilution from a freshly prepared saturated calcium hydroxide solution will give a final solution with approximately 9–10 mg/L of Ca and pH of 8–8.5.

pH>8.5

For artifacts that can tolerate high alkalinity (e.g. papers or textiles with no alkali-sensitive colorants or coatings, and those that are new or in very good condition), imparting an alkaline reserve is the best way of protecting the artifact from aging. The bicarbonates are more soluble; also a solution saturated with CO_2 (unpressurized) is not alkaline, it only becomes alkaline as it dries. For some treatments this may be important. Calcium bicarbonate *(sat. ~360 mg/L)* is much less soluble than magnesium, but the final pH is also slightly lower. For treatment of iron-gall ink corroded papers, this may be a determining factor. magnesium bicarbonate can cause some papers to darken or turn yellow, but it also leaves a much higher alkaline reserve because of higher solubility *(>3000 mg/L)*. Calcium hydroxide *(sat.~900 mg/L)* has the highest pH. Its absorption by paper is also the highest, and therefore it is most effective in neutralizing acids. All three chemicals have their advantages and disadvantages. The final choice will depend on the susceptibility of the artifact (assessed from pre-treatment testing) and the judgment and preference of the conservator.

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