Notes and Communications

Effect of Alkali on the Long-Term Stability of Paper Fibres Containing Lignin

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Introduction

For many years, the archival community in Canada has been concerned about the embrittlement of their paper collections. In large part, the cause of this paper deterioration is acid, which damages paper by speeding up the chemical break-down of cellulose, the major structural constituent of paper fibres. Paper conservators have dealt with this problem through solubilization of acid by water-washing or by neutralization of the acid. However, the effect of these treatments on the stability of paper fibres has not been well understood. Indeed, there are many gaps in our knowledge of the fundamental processes taking place during conservation treatments. This lack of a solid foundation has made it very difficult to devise treatment protocols with adequate certainty about what is best for the paper.

The task of investigating the best way to carry out a specific conservation treatment (in this case, the removal of acid from paper) is best done by examining particular procedures that are in common present-day use. Neutralization of acid is typically carried out by treating the papers with solutions containing alkaline calcium or magnesium compounds. Use of high concentrations of alkali (over 200 ppm) results in the deposition of a buffer reserve, which can serve as protection against future acidification of the material.

In most cases, the alkaline treatment procedures give good results with no visible damage to the artifacts. However, both aqueous and non-aqueous treatments occasionally can cause undesirable visual changes. Most of these alterations involve colour change and, in particular, the yellowing of poor quality paper fibres.

These observations led us to investigate the effect of low concentrations of calcium bicarbonate on naturally-aged cotton fibres. The results showed a destabilization of the fibre by the alkali relative to untreated or wash control samples.[1] Added to these disturbing findings were the many requests that we were receiving from the preservation community for more information and better recommendations for the use of deacidification-type procedures. A survey of Canadian conservators made it clear that the first priority of the Canadian Conservation Institute's (CCI) for research in the paper area should be an investigation into the effects of alkalization on cellulosic fibres. A short time later, the Conservation Committee of the Canadian Council of Archives asked CCI to carry out an investigation of possible problems with the alkalization of paper. They provided funding for chemicals and for a contract chemist to work on the project. Throughout the research they have also provided valuable assistance in the form of comments and suggestions concerning the needs and interests of the archival field.

In the first set of experiments this potential for damage by alkali (i.e. alkaline sensitivity) was examined through the study of thirteen papers. A number of conclusions concerning these papers were drawn from this initial survey: 1) the permanence of the rag and lignin-free papers tested was increased by alkalization; 2) the permanence of ligneous paper was found to be decreased by alkalization; 3) the addition of low concentrations of magnesium sulphate increased the permanence of all papers tested; 4) the beneficial or detrimental effect of the alkaline treatment tended to increase with increasing alkaline concentration; and 5) pure water washing increased the permanence of some papers when it removed destabilizing components such as sodium; however, pure water also decreased the permanence of certain papers when it removed stabilizing compounds already in the paper such as magnesium. These observations were published in both the archival and conservation literature.[2,3]

In a second set of experiments, the role of lignin in the deterioration of paper during alkaline treatment was studied. The following general conclusions were made from this work: 1) alkalization increased the permanence of all the papers studied; 2) in general, the permanence of the papers studied increased with increasing salt concentrations; and 3) high levels of magnesium sulphate appeared to have an adverse effect on the papers by destabilizing the fibres.

The apparent contradiction between the results from these two sets of experiments, with regard to the alkaline sensitivity of ligneous paper, suggests that more data is required in order to make any conclusions concerning the effect of alkali on the stability of ligneous fibres.

The results of the first two studies showed that papers that did not benefit from alkalization were free of alum sizing and were naturally aged. This was particularly evident in the first set of experiments. Papers that did benefit from alkaline treatments were either sized with alum/rosin or were new unsized material. This is not surprising, as alum/rosin sizing is acidic and these types of papers tend to be low in calcium, which is a beneficial agent for stabilizing cellulose fibre.

This article is a summary of the latest experimental work devoted to the effect of alkali on the long-term stability of ligneous cellulose fibres. In particular, the project investigated the role of sizing and chemical additives in relation to the effect of alkali on ligneous materials. As described below, six ligneous papers and three lignin-free control papers were studied. The procedures under study are as follows: alkaline magnesium bicarbonate solutions (20, 200, and 2000 ppm magnesium; 20 ppm corresponds to a low washing concentration; 200 ppm, a medium washing/light deacidification concentration; and 2000 ppm, a high full deacidification concentration) and neutral pH magnesium sulphate (20 ppm magnesium corresponding to a low washing concentration). Appropriate controls were included: "no treatment" and "wash only" samples. An article containing the full numerical data will be published elsewhere.

Materials Studied

The papers used in this study were drawn from material donated from various archival institutions across Canada as well as CCI's didactic collection. These papers were chosen by the authors because of their availability and homogeneity, as well as for their chemical attributes, such as the presence of aluminum, rosin, or lignin and the degree of polymerization. A discussion of the screening process employed in the selection of papers for investigations carried out at CCI, is available in the literature.[4] A summary of the papers included is given in **Table 1**, along with pertinent data concerning age, fibre, and size content.

Table 1: Papers Included in the Investigation

Paper	Date	Fibre	Size	Format
P1	1920	ligneous wood	unsized	book
P2	1952	ligneous wood	unsized	scrapbook
P3	1955	ligneous wood	unsized	book
P4	1908	ligneous wood	alum/rosin	book
P5	1927	ligneous wood	alum/rosin	book
P6	1952	ligneous wood	alum/rosin	book
P7	1886	lignin-free wood pulp	unsized	book
P8	1907	lignin-free wood pulp	alum/rosin	book
P9	1992	cotton	starch	off-set

Papers P7, P8, and P9 were chosen as control papers; the data for these papers should aid in the interpretation of the results for the ligneous papers.

Treatment of Papers

The nine papers described in **Table 1** above were treated with aqueous solutions commonly used in conservation treatments designed to remove acid from paper fibres. The water used in all of the process sequences was purified by being passed through a carbon filter, Millipore "Milli-RO 10 Plus" reverse osmosis, and

Millipore "Milli-Q Plus" polisher. Each paper received six different chemical treatments. A summary for the labelling system used is given below; it includes all the treatments carried out as well as appropriate control samples.

C1 -	untreated paper control
C2 -	paper washed with water only (wash control)
20S -	paper treated with 20 ppm magnesium sulphate solution
20C -	paper treated with 20 ppm magnesium bicarbonate solution
200C -	paper treated with 200 ppm magnesium bicarbonate solution
2KC -	paper treated with 2000 ppm magnesium bicarbonate solution.

Paper samples, except C1 (untreated control), were immersed in pure water for ninety minutes. The C2 sample was removed and dried after washing. The other samples were soaked in four litres of the appropriate treatment solution. The ratio of paper (grams) to chemical solution (millilitres) was 1 to 1500. After fifteen minutes, the samples were placed in a fresh bath containing another four litres of solution. This was repeated two more times to give a total of four fifteen-minute treatments (sixty minutes and sixteen litres of solution). The sixty minute time period represents an extensive treatment; thin and/or absorbant papers may not require this extended length of time.

The alkaline solutions used in this procedure contain magnesium in the form of a colourless, water-soluble bicarbonate salt. During immersion of the paper in the solution, the fibres absorb both magnesium and bicarbonate species. During drying, the bicarbonate species is changed by the carbon dioxide in air into a white, sparingly water-soluble salt, magnesium carbonate. This compound does not migrate in the sheet of paper, but will react with any acid that migrates to any site where the carbonate is located.

The long-term effects of the various treatment sequences were investigated through the analysis of samples before and after artificial aging for four weeks at 80°C and 50 per cent relative humidity. Aging took place inside a moisture controlled oven (Despatch LEA-1 69): the paper samples were hung separately and secured to stainless steel racks in the oven using nickel/chromium wire.

Analysis of Papers

Eight different types of analytical data were collected for all samples, unaged and aged. The analyses are described below, along with comments concerning their value in this study.

Average Degree of Polymerisation (DP)[5,6,7,8]

The average DP was determined using a viscometric procedure. The data collected is an estimation of the average length of the cellulose chain that makes up the main structural component of the paper fibre. As part of the degradation process, the chains are broken, which causes a drop in average length. Fibre strength and durability is very dependent on the length and state of degradation of the cellulose molecules; lignin contributes significantly less to the strength of the paper sheet. Degree of polymerisation is one of the most useful methods for following change in paper, as it is very sensitive and can be used for papers of an extremely wide range of degrees of degradation. In drawing conclusions regarding permanence issues raised in this project, most weight has been given to the DP data.

Zero Span Tensile Strength[9,10,11]

Zero-span tensile strength is a physical test that measures the intrinsic strength of fibres (intrafibre bonding, i.e., the cohesive strength of individual fibres) as well as the strength of the adhesive bonds between fibres (interfibre bonding). When the samples are wetted prior to analysis, the interfibre bonding is diminished and the measured strength is mainly dependent on the intrinsic strength of the fibres that make up the sheet. As degradation proceeds, zero-span strength decreases. The measurements carried out for this investigation were performed using a TroubleShooter Pulmac Instrument.

Cold Extraction pH[12]

The level of acidity of paper can be measured by soaking samples in very pure water. Water-soluble acids are extracted and the pH of this extract is measured. Values below 6.0 usually indicate an acidic paper; values above 7.2 show that alkaline material is present; neutral paper (neither acid or alkaline) is between pH 6.0 and 7.2. The pH data give a semi-quantitative estimation of how much acid or alkali is in the paper. This method of pH measurement was chosen in preference to surface pH because the extraction of the paper measures the acidity of both the interior and surface of the sheet. In addition, the relatively large sample size (three replicates of one gram each) tends to give a good average indication of pH for paper samples that are heterogeneous. As acid paper usually degrades more rapidly than neutral papers, pH can give some indication of expected rates of degradation of specific samples.

Alkaline Reserve[4,13]

Alkaline reserve is a measure of the amount of material in a paper that is capable of neutralizing acids. It is an excellent method for monitoring the amount of calcium or magnesium carbonate that is deposited into paper during deacidification and alkalization of fibres. The procedure used for determining alkaline reserve was a ASTM standard procedure, modified to give more accurate data.

Magnesium Determination by Flame Atomic Absorption Spectroscopy[14,15]

Flame atomic absorption spectroscopy (AAS) was used in this study for the determination of magnesium only. However, it is capable of quantitative determination of numerous other inorganic materials (e.g., iron, copper, calcium, sodium, etc.). Flame AAS is an accurate technique which suffers from few interferences. The instrument used for analysis was a Philips's Pye-unicam PU 9000 Atomic Absorption Spectrometer.

Thickness, Density, and Water Absorbency[16,17,18]

Thickness, density, and water absorbency are basic properties of paper which help to characterize it. These measurements were performed on the untreated control samples in order to learn if any correlation could be drawn between them and sensitivity to alkali. The thickness of the paper was measured using a manually-operated calliper-type instrument. Density measurements were calculated from weight, calliper, and area data. A modified water absorbency test, similar to the TAPPI Standard T 432 om-87, was performed on each of the papers.

Results and Discussion

All of the conservation treatments described in this article involved washing papers with water containing magnesium salts. These treatments can change two fundamental characteristics of the papers: composition, in particular the inorganic content; and long-term stability (i.e., permanence), determined by comparison of chemically-treated materials with control samples (no treatment or only washing with pure water).

Effect of Treatment on Composition of Paper

Alteration of the composition can be monitored by determining the quantity of a particular material before and after treatment. The concentration of magnesium (or calcium), acid, and alkali (buffer) are three important variables in paper that affect permanence. The amounts of the various materials were determined by flame atomic absorption spectroscopy (magnesium content), estimation of alkaline reserve (alkali concentration), and cold extracted pH (acid or alkali concentration).

Figure 1 shows a plot of all of the data for treatment of P1 to P6 (C2, 20C, 200C, and 2000C), with magnesium content of the treated paper on the vertical axis and alkaline reserve of the treated paper on the horizontal. A good straight-line relationship was found to exist between magnesium concentration in the treatment bath and the alkaline reserve (expressed as per cent by weight magnesium carbonate) of samples treated with magnesium bicarbonate. As the concentration of magnesium in the treatment bath increased, so did the quantity of elemental magnesium and the alkaline reserve. All of the ligneous papers (P1 to P6) had low initial values for both alkaline reserve and magnesium. The fact that all of the different ligneous papers could be plotted on the same graph indicates the great similarity in how they absorb magnesium (and hence alkali) from the wash water.

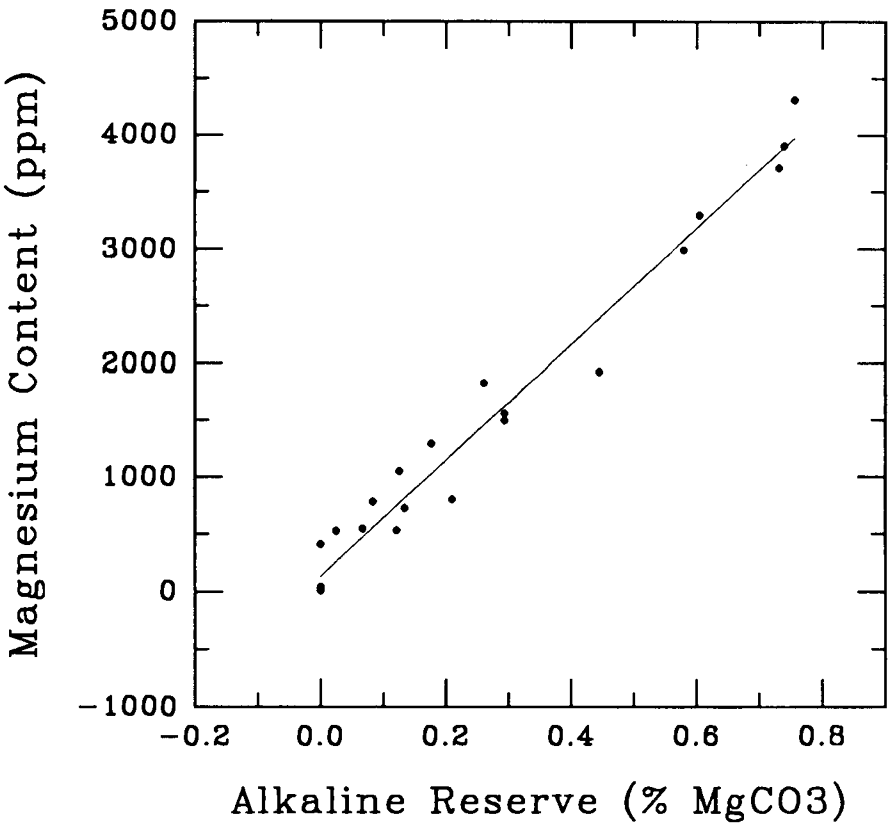
Given the results shown in **Figure 1**, it is likely that a plot of pH versus alkaline reserve also will show a straight-line relationship. The data for P1—an unsized, ligneous paper dated 1920—are given in **Figure 2**. A good straight-line relationship is illustrated. However, it is very interesting to note that the pH is on the acid side (less than 7.0) at lower alkaline reserve values.

In order to explain how the pH can be acidic in the presence of an alkaline buffer, it is necessary to look more closely at the tests that were carried out. The cold extracted pH measurement is performed by immersing small pieces of the paper in pure water over a relatively short period of time (one to two hours). The pH value obtained is indicative of what material can be extracted under these rather mild conditions. In other words, the acid is readily solubilized while the magnesium is not.

The problem of the insolubility of the magnesium carbonate is dealt with by a rigorous procedure that measures both buffer salts and acid. The "alkaline reserve"

Figure 1

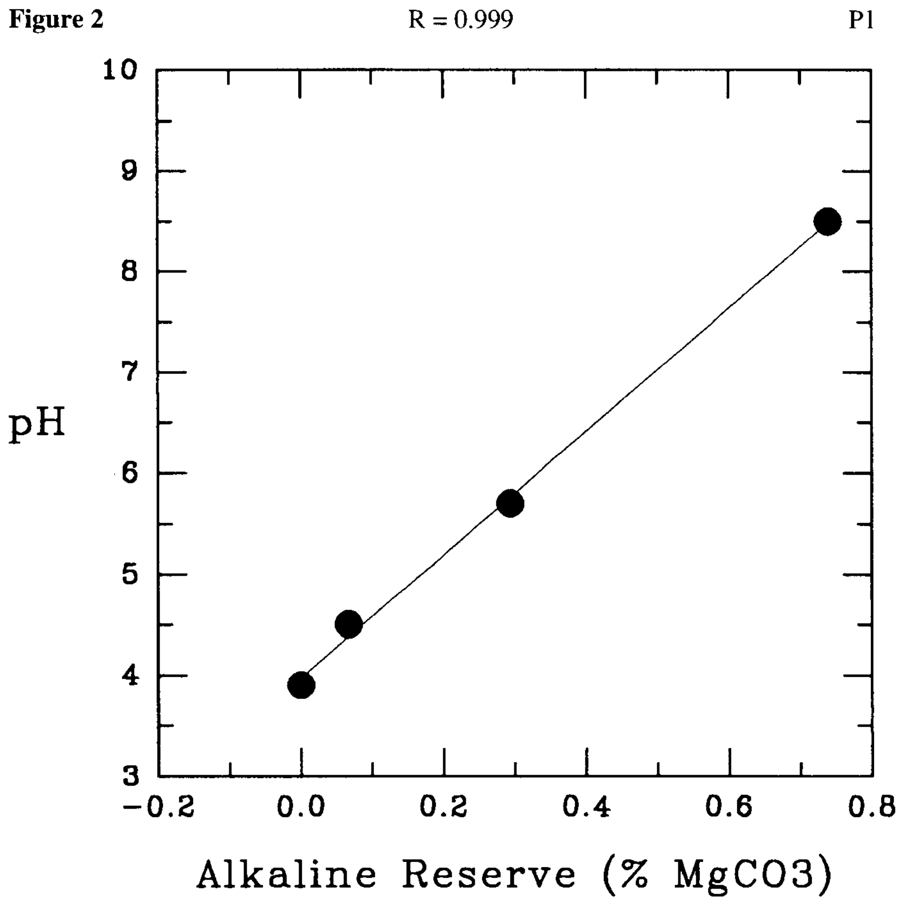
R = 0.986
P1 to P6



The effect of concentration of magnesium bicarbonate in the wash water (ppm magnesium) on the amount of alkaline reserve (% magnesium carbonate) deposited in the paper fibres; results are plotted for all six ligneous papers (P1 to P6).

method used in these studies involves solubilization of the carbonate by reaction with acid over a lengthy sixteen-hour extraction time. Acid not consumed by reaction with carbonate is measured along with any acid present in the original sample. Comparison of this value with the concentration of acid added to the paper gives data corresponding to the net quantity (alkaline reserve minus acid present in sample) of buffer reserve. In the case of the ligneous papers, significant buffer reserve was observed mainly with the 200C and 2000C samples. (Note: At these concentrations of magnesium bicarbonate, it would be unusual to observe residues of magnesium carbonate on the surface after drying.)

Figure 2



Comparison between the pH and alkaline reserve content (% magnesium carbonate), of samples of P1 (1920 unsized ligneous paper) washed in various concentrations of magnesium bicarbonate.

Evaluation of the cold extracted pH values and the alkaline reserve data makes it apparent that the P1 sample shown in **Figure 2** contained both acidic and alkaline material. With samples treated with low concentrations of magnesium bicarbonate in the wash water (20 and 200 ppm), the simple pH extraction solubilized acid but little alkali. At the highest magnesium concentration (2000 ppm) treatment, there was proportionately more alkali present in the fibres and the pH value obtained was alkaline (above 7.0). When the alkaline reserve procedure was carried out, it was possible to extract and neutralize all of the alkali; the answer obtained was the amount of alkaline reserve present *minus* the amount of acid present.

Two important conclusions can be drawn from the above observations. The first is that pH is not always a good indication of the overall acidity or alkalinity of a paper. The second is that acidic and alkaline materials can exist at the same time in paper. During immersion of paper in a magnesium bicarbonate solution, alkali is deposited in the fibres at the same time as acid materials are being neutralized. Therefore, in order to completely neutralize all of the acidity in paper, it may be necessary to deposit a small buffer reserve. This may be more true for ligneous material than for non-ligneous, as the lignin is present in the paper as discrete particles. These ligneous fibres probably contain a large share of the acid and hence may take more time to be neutralized. In addition, it may be necessary to use a higher concentration of alkali than that required by the less acidic non-ligneous portions of fibres.

Permanence of Papers Washed With Alkaline Magnesium Bicarbonate Solutions

The various paper samples were examined in an effort to determine whether alkalization of individual papers was increasing or decreasing the rate of degradation of the fibres. Degradation can be followed by any analytical method which monitors a property that is unequivocally linked to a degradative process. For example, change in degree of polymerisation (DP) directly measures chemical change; alteration in zero span tensile strength directly measures physical change. There is some correlation between DP and zero span tensile measurements as chemical change eventually results in loss of strength. However, physical measurements are complex and are influenced by many factors, including length of fibres, type and amount of sizes and fillers used in the papermaking, density and thickness of the sheet, and ambient temperature and humidity. Also, physical changes (as measured by individual physical tests) do not occur over the entire lifetime of a sheet of paper, e.g., decrease in fold endurance can be most evident when the sheet is relatively undegraded and loss of zero span tensile strength is rapid when the paper is more chemically degraded.

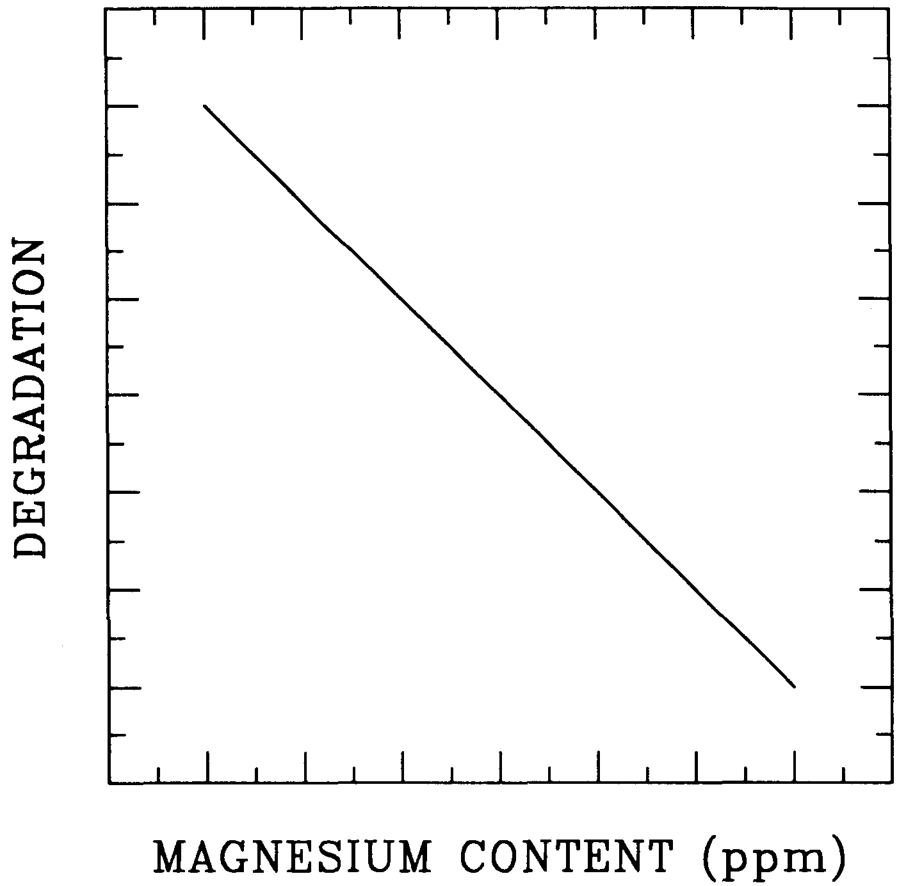
In order to interpret the results of this investigation it is necessary to consider the possibility of individual papers exhibiting only positive effects of alkaline treatment or only negative effects of alkaline treatment or a mixture of the two. A simple representation of these three theoretical possibilities is given in **Figures 3, 4, and 5**.

Figure 3 shows a typical example of a paper which is improved by alkali. The degradation (as measured by any change in any important chemical or physical property) decreases as the concentration of magnesium in the wash water increases. All of the alkali-treated material will degrade more slowly than the control samples that were only washed or not untreated. The graph shown in **Figure 4** illustrates the opposite case in which the paper is being destroyed by alkali deposited during washing. The rate of degradation increases with the concentration of magnesium used. The samples treated with alkali degrade faster than the 'no treatment' or 'wash only' control papers.

A third possibility is that both processes could occur at the same time:

1. degradation is slowed down by the beneficial presence of alkali, which neutralizes the acids that form during aging, and 2. degradation is sped up by the detrimental presence of alkali, which directly breaks down the paper fibres over time. If the two processes are perfectly balanced, changing the concentration of the alkali would not affect the rate of degradation (see **Figure 5**). The alkaline-treated

Figure 3

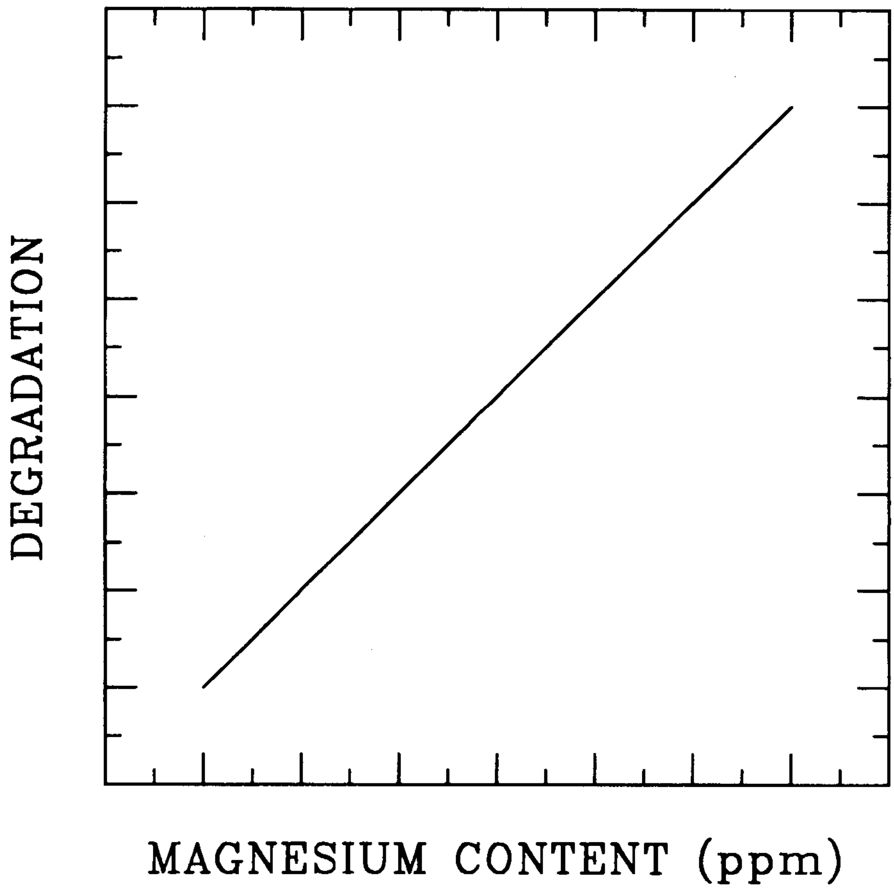


The beneficial effect of adding alkaline magnesium bicarbonate to wash water used in treatment of paper; degradation goes down as concentration of magnesium increases.

samples would have similar stability as in the wash control. However, the degree of alkaline sensitivity could vary greatly among papers. Similarly, some papers produce more acid during aging than the norm (e.g., ligneous or significantly oxidized fibres); these papers may benefit especially from treatment with alkali.

The results for the nine papers tested in this investigation have been interpreted with the above points in mind. **Table 2** summarizes some conclusions regarding degradation as a function of concentration of magnesium carbonate, using the DP results to monitor degradation. The comparison between C1 and the magnesium-treated samples gives information concerning gain or loss of permanence when

Figure 4

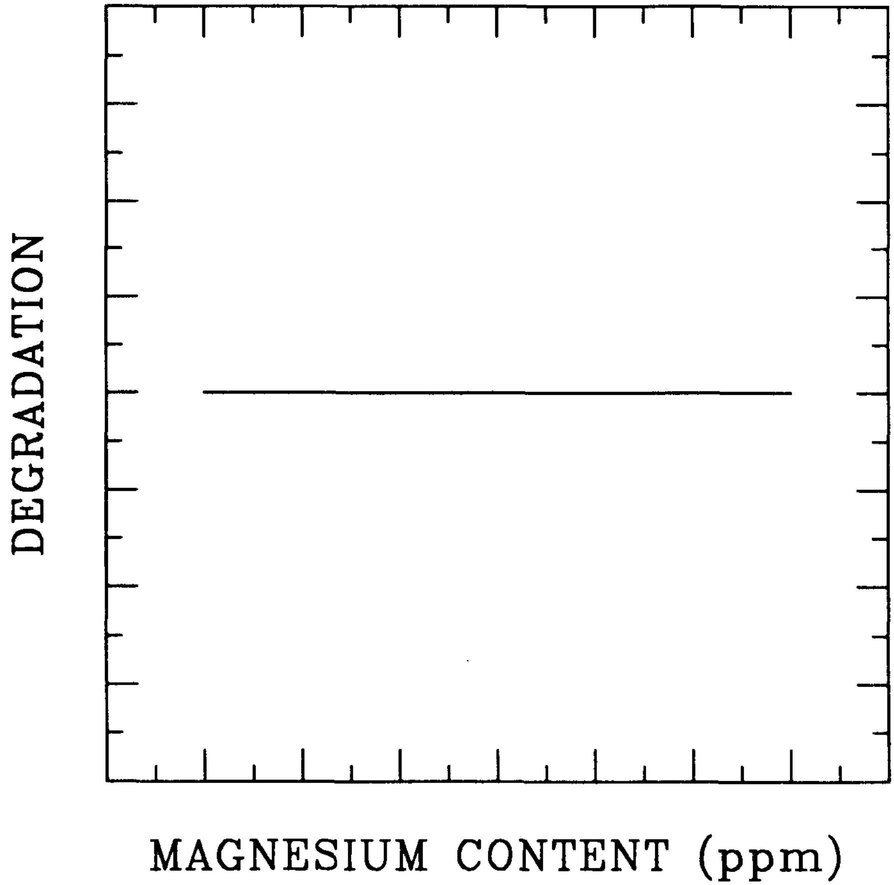


The detrimental effect of adding alkaline magnesium bicarbonate to wash water used in the treatment of paper; degradation goes up as concentration of magnesium increases.

considering no treatment at all versus the alkalization procedures. Comparing C2 and the magnesium bicarbonate samples gives insight as to whether adding alkali to the wash water is beneficial or detrimental. Looking at the trend among the magnesium samples (i.e., increase or decrease in stability as concentration goes up) gives further information about the effect of magnesium treatments on long-term stability.

Seven of the papers (P2 to P8) showed the benefits of washing with solutions of magnesium bicarbonate. P4 is a good example of how degradation can slow down as the magnesium concentration goes up (see **Figure 6**). Occasionally one may see

Figure 5



Combination of beneficial and detrimental effects of adding alkaline magnesium bicarbonate to wash water used in the treatment of paper; degradation not affected by concentration of magnesium.

situations where there is not a steady improvement in papers when the alkali concentration increases. For example, The 20C sample for P5 was more permanent than 200C. In these cases, alkaline sensitivity is probably contributing somewhat to the overall stability of the paper.

The zero-span tensile strength data are inconclusive, as the changes in strength were relatively small and hence not statistically reliable. These span tensile strength measurements are considerably less sensitive to degradation than is degree of polymerisation. Therefore, further aging would have been necessary in order to show significant differences among the samples using this analytical method.

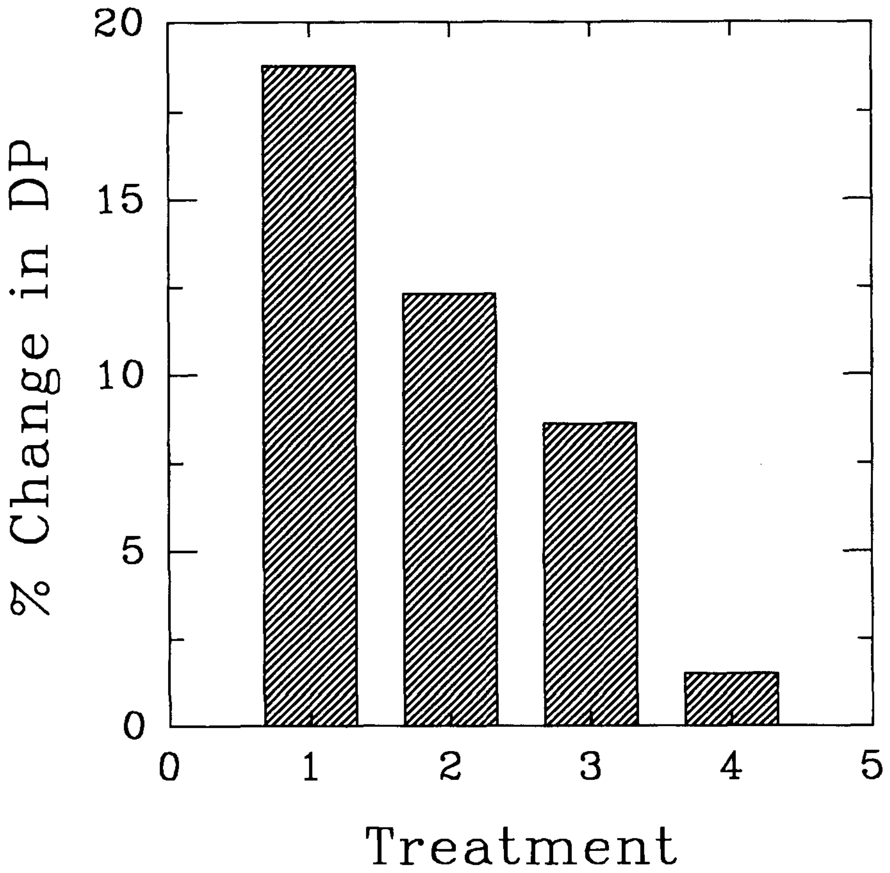
Table 2: Degradation of Paper as a Function of Concentration of Alkaline Magnesium in the Wash Water* Using Degree of Polymerisation Data

Paper	C1 Compared With Magnesium Samples	C2 Compared With 20C, 200C, & 2KC	Conclusion
P1 unsized lignin	C1 more stable	C2 more stable, no increase in stability with magnesium	alkaline sensitivity
P2 unsized lignin	C1 less stable	C2 less stable, increase in stability with magnesium	no sensitivity
P3 unsized lignin	C1 less stable	C2 less stable, increase in stability with magnesium	no sensitivity
P4 sized lignin	C1 less stable	C2 less stable, increase in stability with magnesium	no sensitivity
P5 sized lignin	C1 less stable	C2 less stable, 20C better than 200C	sensitivity slight or not present
P6 sized lignin	C1 less stable	C2 less stable, increase in stability with magnesium	no sensitivity
P7 sized no lignin	C1 less stable than 200C and 2KC	C2 less stable, increase in stability with magnesium	no sensitivity
P8 sized no lignin	C1 less stable than 200C and 2KC	C2 less stable, increase in stability with magnesium	no sensitivity
P9 sized cotton	C1 more stable	C2 less stable, decrease in stability with magnesium	alkaline sensitivity

* Abbreviations for various controls and treatments are given as follows:

C1 = Untreated control
C2 = Wash only control
20C = washed with 20 ppm magnesium
200C = washed with 200 ppm magnesium
2KC = washed with 2000 ppm magnesium

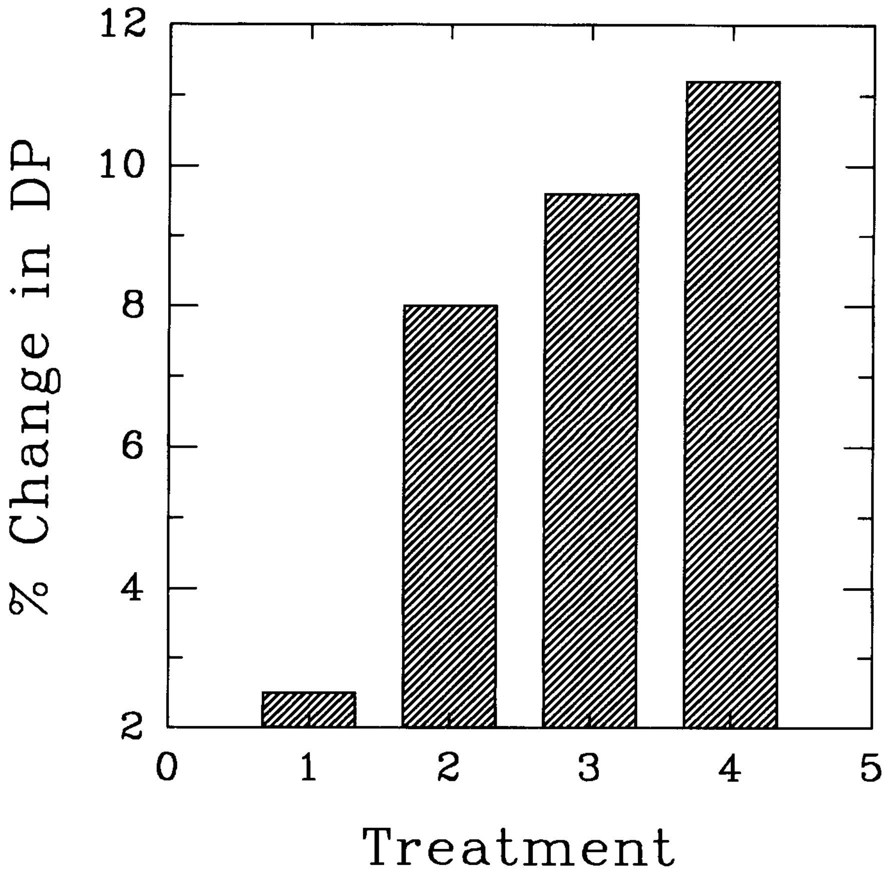
Figure 6



The beneficial effect of adding alkaline magnesium bicarbonate to P4, a 1908 alum/rosin sized ligneous paper, as shown by per cent change in DP (degree of polymerisation); treatment 1 = wash only; 2 = 20 ppm magnesium in wash water; 3 = 200 ppm in wash water; and 4 = 2000 ppm in wash water.

The control samples, C1 (untreated) and C2 (water-washed only), for two papers, P1 and P9, were more stable than samples treated with magnesium bicarbonate solutions. This suggests that alkalization of these papers has resulted in some loss of stability. For P1, permanence did not steadily decrease as magnesium concentration went up, thus suggesting that alkaline sensitivity was partially mitigated by the benefits of the magnesium treatments. For P9, there was a significant decrease in permanence as the alkali concentration went up. This is a clear case of alkaline sensitivity (see **Figure 7**).

Figure 7



The detrimental effect of adding alkaline magnesium bicarbonate to P9, a 1992 starch sized cotton paper, as shown by per cent change in DP (degree of polymerisation) during accelerated aging; alkaline sensitivity is demonstrated. Treatment 1 = wash only; 2 = 20 ppm magnesium in wash water; 3 = 200 ppm in wash water; and 4 = 2000 ppm in wash water.

It is very difficult to be certain about which types of paper are likely to be sensitive to alkali. However, it is likely that a number of characteristics can predispose a paper to alkaline sensitivity. For example, one probable factor is density; another is type and amount of size. P1 has the lowest density of all the samples tested; it was unsized, thus improving contact between fibre and magnesium solution. P9 is a thin paper sized with starch, a carbohydrate material which is very hydrophillic and may increase the level of chemical interaction possible between fibre and magnesium solution. Another important factor is the degree of degradation. Degraded, highly oxidized fibres react with alkali in a manner that leads to breakdown of the cellulose chains, and further degradation.

It is significant to note that lignin does not cause alkaline sensitivity directly. That is not to say that it cannot be a contributing factor. Old ligneous papers are often more degraded than well-processed wood or rag materials of the same era. Some grades are unsized and can be quite porous. However, the work presented in this article, as well as previous research,[2,3] shows that it is possible for lignin-free papers to show alkaline sensitivity. In this earlier work a thin porous linen paper was shown to degrade rapidly when alkali was added to the wash water. Two porous ligneous papers from the same set of experiments also had exhibited slight alkaline sensitivity.

The recognition that alkali can damage paper or image areas causes some serious problems in deciding on an appropriate treatment plan. If significant dirt and/or acid is present, the conservator may want to perform some water washing (providing the image is not soluble in water and the paper is strong enough to withstand wet treatment) in order to remove the detrimental material. Pure water washing has fallen into disrepute with the realization that this removes calcium and magnesium from the fibres and hence causes a loss of permanence.[1,19,20] Comparison of the C1 and C2 control data in this study showed that four of the nine papers decreased in stability when washed in pure water. The conclusion at the end of these observations is that when an artifact has some alkaline-sensitive component, it may be desirable to add magnesium (or calcium) to the wash water in the form of a neutral pH salt. Magnesium sulphate was chosen for this purpose.

Permanence of Papers Washed With Neutral Magnesium Sulphate Solutions

The effect of adding 20 ppm magnesium (sulphate) to water was studied in this project. The results are summarized in **Table 3**. When comparing the effect of adding magnesium sulphate to the wash water versus not doing anything at all (C1 sample), six out of nine of the papers were helped by treatment with magnesium sulphate. The sulphate samples were also compared with the wash control, C2, and the magnesium carbonate treated material. The sulphate-treated papers were more stable than C2 for four papers (P3, P4, P5, and P6), equally stable for three papers (P7, P8, and P9), and less stable for two papers (P1 and P2). Magnesium sulphate treated material was less stable than those treated with magnesium bicarbonate eight times out of nine. The one exception is P9, which exhibited marked alkaline sensitivity.

Sulphate treatments can be very useful in cases where alkaline sensitivity is expected. In particular, its use is indicated when pH-sensitive dyes, inks, and colourants are present on the paper being treated (e.g., iron gall ink in manuscripts and Prussian blue pigments in blue prints). However, it is important to note that some of the papers were made less permanent by magnesium sulphate. At the same time, it must be acknowledged that these problems with the sulphate were not noted in the previous work, which centred on lignin-free (mostly rag) papers. Because ligneous papers are more chemically complex than rag papers, predictions are significantly more difficult to make. It is possible that the sulphate anion destabilizes lignin-containing fibres in some manner. It would be interesting to compare the effect of magnesium sulphate with that of other neutral pH salts such as magnesium chloride.

Table 3: Effect of Addition of Magnesium Sulphate to Wash Water*

Paper	Stability of C1 Compared With Sulphate Sample	C2 and Carbonate Samples Compared With Sulphate Sample
P1	C1 more stable	sulphate less stable than C2 & carbonate
P2	sulphate more stable	sulphate less stable than C2 & carbonate
P3	sulphate more stable	sulphate more stable than C2, less stable than carbonate samples
P4	sulphate as stable as C1	sulphate more stable than C2, less stable than carbonate samples
P5	sulphate more stable	sulphate more stable than C2, less stable than carbonate samples
P6	sulphate more stable	sulphate more stable than C2, less stable than carbonate samples
P7	C1 more stable	sulphate as stable as C2, less stable than carbonate samples
P8	C1 more stable	sulphate as stable as C2, less stable than carbonate samples
P9	sulphate more stable	sulphate as stable as C2, more stable than carbonate samples

* Abbreviations for control samples are as follows:
C1 = Untreated control
C2 = Wash control

Summary of Conclusions

1. A relationship exists between magnesium bicarbonate concentration in the wash water and the quantity of alkaline reserve (expressed as per cent by weight magnesium carbonate) in samples treated with magnesium bicarbonate. As the concentration of magnesium in the treatment bath increases, so does the quantity of elemental magnesium and the alkaline reserve.
2. Cold extraction pH values are not always a good indication of the degree of acidity or alkalinity of a paper. Acidic and alkaline materials can exist at the same time in a single sample of paper.
3. Two papers, P1 (1920 unsized ligneous) and P9 (modern starch sized cotton), are degraded by alkali treatment: that is, the control samples, C1 (untreated) and C2 (water washed only), for these two papers are more stable (as indicated by degree of polymerisation data) than samples treated with the magnesium bicarbonate solutions. For P1, permanence does not steadily decrease as magnesium concentration goes up, thus suggesting that alkaline sensitivity is partially mitigated by the benefits of the magnesium treatments. For P9, there was a significant decrease in permanence as the alkali concentration went up.
4. The other seven papers, P2 to P8, show the benefits of washing with solutions of magnesium bicarbonate.
5. Lignin does not cause alkaline sensitivity directly. However, it may be a contributing factor.
6. Only one paper, 1920 unsized ligneous P1, treated with neutral pH magnesium sulphate, is less stable than both of its controls, C1 and C2. Six out of nine of the papers (P2, P3, P4, P5, P6, and P9) are more stable than the "no treatment" control; four papers, P3, P4, P5, and P6, are more stable than the "wash only" control; three papers, P7, P8, and P9, are as stable as the "wash only" control; two papers, P1 and P2, are less stable than the "wash only" control.
7. Eight times out of nine, magnesium sulphate treated material is less stable than those treated with magnesium bicarbonate. The one exception is P9, modern, starch-sized cotton, which exhibits marked alkaline sensitivity.

Impact on the Conservation Treatment of Archival Collections

In the past, there has been a general assumption in the preservation field that treatments to remove acidity from paper will have a positive impact on the permanence of the material. The first indication that this point of view has some problems came when researchers began to observe loss of permanence of some papers that had been washed with pure water.[1,3,19,20] Now, alkaline magnesium (or calcium) treatments, are shown to damage some papers. All of these results are important, as they show the great diversity of naturally-aged materials and how they react when being treated. The concept of mass treatments for a varied collection becomes problematic as we recognize that there is a potential for these "beneficial" treatments to damage paper.

At the same time, it is important to remember that a large portion of Canadian archival collections contain significant amounts of acid and are undergoing rapid embrittlement. It is difficult to justify doing nothing in fear of damaging some artifacts. Instead, it is necessary to carry out treatments where they are warranted by obvious signs of instability. At the same time, however, it is important to have some type of screening process. This is especially critical when the artifacts to be treated are very valuable and/or heterogeneous.

A decision regarding whether to treat a specific artifact is complex and must be made with input from a trained paper conservator. Such things as extent of degradation of the paper support, solubility and pH sensitivity of media, the presence of seals and other additions, as well as the format of the item will be important.

Probably the best way to decide if wet neutralization or alkalization treatments are justified is to take the surface pH of the document. While this article points out some difficulties with pH measurements, they still remain our only non-destructive and relatively quick analytical method for obtaining information on degree of acidity. The next obvious question is: when is the pH low enough to warrant treatment? Some guidelines are as follows:

a) Alkaline or neutral pH papers will not require neutralization or alkalization procedures. Alkalinity may be considered to be pHs of 7.3 or higher. Neutral papers fall into the range of pH 6.0 to 7.2. The water used to take the pH measurement impacts on the observed pH of paper; even very pure water can be close to pH of 6.0.
b) Mildly acid papers (pH 5.0 to 6.0) will probably benefit from neutralization and alkalization. The need, however, must be balanced against the risk to media.
c) Papers in the range of pH 4.0 and 5.0 contain significant acid and should be treated if possible.
d) Papers below pH 4.0 probably contain some mineral acids from very acidic air pollution (e.g. sulphuric acid). Without some neutralization of this acid, degradation will be extremely rapid.

Once the decision has been made that a neutralization or alkalization treatment will be carried out, it is necessary to make some decisions regarding what procedure to follow. Based on the results obtained in this project, in addition to our previous work,[3] we would make the following recommendations for the treatment of acidic, naturally-aged papers:

1. On balance, washing with only pure water cannot be justified, as there is a strong possibility (over 50 per cent) that the paper will become less stable than if no treatment were carried out.
2. Papers that are very thin, absorbent, and/or degraded may be at risk if treated with alkali. Low concentration magnesium bicarbonate (around 20 ppm) can be justified if the paper is extremely acidic (pH less than 4.5). In most cases, however, the preferred choice would be 20 ppm magnesium sulphate.
3. In cases where the media is sensitive to alkali (e.g. colour change or increased solubility), the best choice would be a solution of 20 ppm magnesium sulphate.
4. Mildly acidic documents in good storage conditions, that are not sensitive to alkali, can be treated with low to medium concentrations of magnesium bicarbonate (20 to 500 ppm magnesium). Larger concentrations of magnesium (1000 to 2500 ppm) are indicated when the acid level is high.

Areas for Future Study

The research discussed in this article answers many of the questions relating to the permanence of paper fibres that have been treated with alkaline chemicals. However, more research remains to be done concerning optimizing process conditions; for example, what is the best concentration of chemical to use and how long should the paper be immersed in a treatment solution in order to achieve the desired degree of acid removal? In addition, there is a great need to learn more about how alkali affects the information or images found on sheets of paper. Colourants such as inks, dyes, and pigments can be extremely sensitive to pH. Changes to them can affect the archivists' ability to retrieve information as well as the intrinsic value of important or rare items.

We also need to know more about how paper that has been neutralized or buffered is affected by exposure to common air pollutants such as sulphur dioxide, sulphur trioxide, nitrous oxide, and ozone. Conversely, does the fact that a paper is severely polluted affect the way that the alkaline treatment should be carried out?

It must also be recognized that concerning the preservation of archival collections, we need more research done in many areas that do not pertain directly to alkalinity questions. Some of the most important concern lignin. In the absence of a buffer, lignin damages paper; is this still true, however, when an alkaline buffer is present? To what extent does lignin increase the rate of absorption of air pollutants into paper? Another significant area concerns storage conditions for collections: What is the permanence of the materials in contact with artifacts, e.g., boxes, tissues, folders, envelopes, etc.? What are the best temperature and relative humidity conditions for paper-based materials? What are the best methods for controlling air pollution in collection storage areas?

The above list is not complete; nor is it meant to represent all of the research needs of the archival field. However, it does point out some areas where we know enough about the problems that we can formulate some questions. This is the first and often the most critical step in carrying out meaningful research.

Notes

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