

## The Role of Electrophilic Metal Ions AluminumIII and MagnesiumII in Paper Degradation and Deacidification

### ABSTRACT

While conservation scientists acknowledge the oxidative degradation of cellulose in paper to be complex, they overwhelmingly present *hydrolysis* as proceeding in just one way in paper degradation, via a proton-catalyzed mechanism. Researchers report in the scientific literature, however, an important additional mechanism of degradation where aluminumIII ( $\text{Al}^{\text{III}}$ ), the metal cation in papermaker's alum, is present. This competing mode of degradation has a differing pH dependence and temperature dependence, thus affecting deacidification measures and influencing accelerated aging tests, respectively.

At the 38th Annual Meeting of the American Institute for Conservation (AIC) in Milwaukee (spring 2010), Heritage Science for Conservation presented an ongoing study targeting these competing reactions. Innovative approaches include systematic incorporation of macromolecular structure and phase interactions into aging studies, and sample formulation techniques that better isolate mechanisms and improve ionic strength and pH control. Results show unambiguous destabilization of samples by  $\text{Al}^{\text{III}}$ , controlling for critical variables including pH. Preliminary pH dependence results suggest that the effect may disappear between pH 5.0 and 6.9, supporting deacidification as an effective means of limiting both mechanisms of degradation. Also suggested is that magnesiumII, though chemically similar to  $\text{Al}^{\text{III}}$ , does not itself catalyze hydrolysis. MagnesiumII is in some deacidification agents, e.g. magnesium carbonate and oxide.

### HERITAGE SCIENCE FOR CONSERVATION

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Hopkins University within the Dept. of Conservation and Preservation, The Sheridan Libraries, whose director, Sonja Jordan-Mowery, is the principle investigator. The senior conservator and coauthor of this article is William Minter. HSC conducts research programs that are ambitious in scope and particularly helpful to book and paper conservation and conservators. Results of the research are disseminated to students as well as conservation, chemistry and materials science, library, industrial, and general audiences. Additional projects presented at AIC 2010 Milwaukee included examinations of leather treatments and dressings; conservation adhesive and paste preparation methods analyzed by light microscopy; and papermakers' sizing methods analyzed after accelerated aging by measuring optical, chemical, and physical properties. These presentations may be viewed on the HSC website (2010), the AIC website (2010), and in this volume of the Book and Paper Group (BPG) Annual.

### INTRODUCTION

Aluminum salts were traditionally applied in Western papermaking to limit gelatin putrefaction and to harden gelatin size (Brückle 1993). While the prevailing use of them during the 19th and 20th centuries for the first major internal sizing—rosin-alum sizing—has now been diminished by alkyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) sizing systems, aluminum salts remain ubiquitous in modern papermaking as retention, drainage, and flocculation aids, to control pH, and to fix resins and dyestuffs (Scott 1996). Commentators explicitly documented the relationship of aluminum salts to poor permanence early in the 19th century (Stanley 1992), and conservation scientists now attribute this degradation primarily to the behavior of water-coordinated  $\text{Al}^{\text{III}}$  as a Brønsted-Lowry acid (W. J. Barrow Inc. 1974; Priest and Farrar 1994). A Brønsted-Lowry acid is any ion or molecule that loses or “donates” a proton,  $\text{H}^+$ . As illustrated in figure 1, protons readily catalyze the hydrolysis of cellulose, and there is no doubt that this mechanism is a significant component of paper degradation in libraries, museums, and archives.

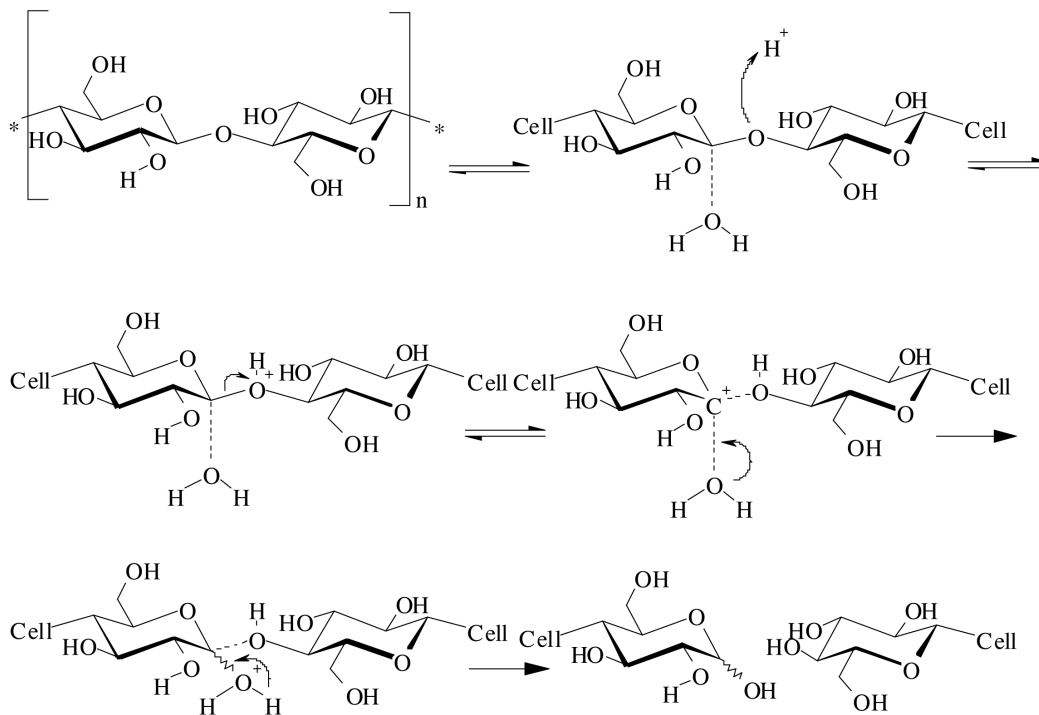


Fig. 1. Proton-catalyzed hydrolysis of cellulose, a.k.a. “acid-catalyzed” hydrolysis of cellulose in paper, originating with protonation of the glycosidic oxygen atom

Periodically, however, reviewers have suggested that the picture is more complex for papers containing  $\text{Al}^{\text{III}}$  salts such as papermaker’s alum. Parks concluded in 1971 that destabilization of cellulose by aluminum sulfate is qualitatively different from destabilization by sulfuric acid, which should not be the case if the  $\text{Al}^{\text{III}}$  is acting exclusively as a Brønsted acid. From a kinetics study, Barański, Dziembaj, and coworkers (2004) concluded that in addition to proton-catalyzed hydrolysis, some other mechanism must be simultaneously at work. Gurnagul, Howard, and coworkers noted in a 1993 review that “it is a matter for some astonishment that we still do not know for certain . . . the exact mechanism by which aluminium compounds affect permanence . . .”

A previous study (Baty and Sinnott 2004; 2005) tested the hypothesis that  $\text{Al}^{\text{III}}$  is directly catalyzing cellulose hydrolysis relevant to paper-based heritage materials degradation. Such catalysis could proceed from the coordination pattern illustrated in figure 2. Notice that the C6'-OH group is well positioned to behave as a second ligand to chelate, “bite,” the  $\text{Al}^{\text{III}}$  in place, though this coordination has not been proven. The 2004–2005 Baty and Sinnott study was prompted by the realization that physical organic chemists have known of an electrophile-catalyzed hydrolysis of glycosides with relatively stable leaving groups (the part of the molecule that breaks off) for some time (Clark and Hay 1970; Clark, Hay, and Dea 1973), although the same hypothesis could equally have been prompted by Popoola’s (1991) observation of enhanced

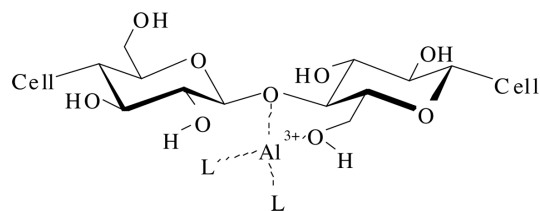


Fig. 2. Proposed coordination of  $\text{Al}^{\text{III}}$  by the glycosidic oxygen and C6' hydroxyl, from which coordination pattern  $\text{Al}^{\text{III}}$ -catalyzed hydrolysis of cellulose in paper could proceed

hydrolysis of cellulose in the presence of iron(III) chloride, enabled by suspected iron(III) coordination with the leaving group. Baty and Sinnott did find efficient electrophile-catalyzed hydrolysis under the conditions tested, but the pH range was limited to where the sample could remain a homogenous aqueous solution (3.0–3.5), avoiding crystal entrapment of either products or reactants preferentially, which would skew results. Further limitations of the study were that while the cellulose model compound mimicked cellulose perfectly in terms of steric and inductive effects around the glycosidic linkage—the site of hydrolysis—it did not incorporate the macromolecular structure that is retained in paper, nor the particular way in which water is present adsorbed onto the paper fibers in heritage collections.

There are also electrophilic metal centers other than  $\text{Al}^{\text{III}}$  that can be present in paper-based heritage collections, and we hypothesize that these may catalyze the hydrolysis of cellulose in a similar way. These other metal ions include magnesiumII ( $\text{Mg}^{\text{II}}$ ) and ironII. In this study we are particularly interested in  $\text{Mg}^{\text{II}}$  because it is present in many compounds such as magnesium oxide and magnesium carbonate that conservators use in deacidification (Baty, Maitland et al. 2010).

## MATERIALS AND METHODS

### Substrates—Macerated and Intact Paper

Overcoming the limitations of previous work to assess the scope of  $\text{Al}^{\text{III}}$  catalysis of cellulose hydrolysis in paper (limited pH range, no macromolecular effects incorporated) must involve the use of a heterogeneous sample—paper itself. Whatman 42 filter paper was used in this study because it was the next gradual step from small molecule studies. Whatman 42 contains the relevant cellulose macromolecular and water sorption properties, but lacks hemicellulose, lignin, and salts that can be found in paper-based heritage collections. These other components and structural features must be added systematically in future experiments to measure their effects against adequate controls.

This research project consists of two phases: (1) The Whatman paper is macerated and aged while immersed in an aqueous mixture. (2) The various compounds of interest are deposited onto the Whatman paper and aged with the amount of water that is adsorbed ( $\sim 5.5\%$ ) at ambient conditions (TAPPI Standard Conditioning Atmosphere (1998)). In the first phase, the ratio of oven-dry equivalent weight paper to aqueous mixture was that of the TAPPI hot extraction pH test method (1.00 g : 70 mL, TAPPI 2002). This TAPPI standard dates to the 1930s and is a key component of the concept of paper pH. By completing the first phase in aqueous mixtures, it was possible to draw the analogy between what was measured in this study and previous small molecule studies. Also, since each replicate was easier to perform in the aqueous system, it helps to identify suitable conditions for aging the paper intact.

### Buffering Systems

In this study, common-ion-effect buffers were used, which hold the pH at a certain set point via Le Chatelier's principle, as opposed to alkaline reserve buffers, which hold the pH at the  $\text{pK}_a$  of the alkaline agents until they are depleted (if ever) by Brønsted acids. Using these buffers (5:1 molar ionic strength buffer : molar anhydroglucose units of cellulose) in this innovative fashion enabled studying paper degradation at a specific pH, rather than allowing the variable of pH to "float" during aging. Since this was an Arrhenius study conducted at elevated temperatures, care was taken to select buffering systems with a low pH dependence on temperature—a low  $\text{dpH}/$

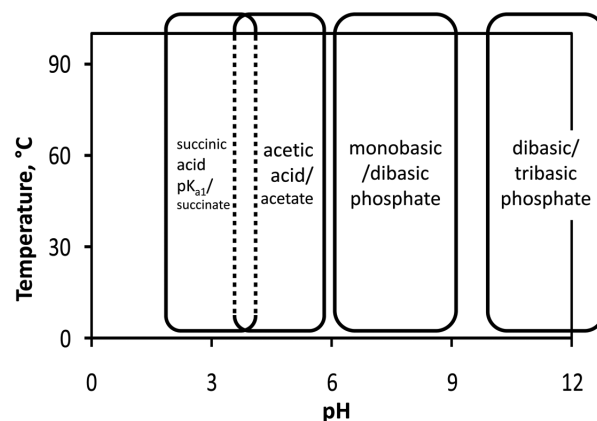


Fig. 3. Useful pH ranges of select common-ion-effect buffering systems

$dT$  (Dawson, Elliott et al. 1986). Figure 3 shows the approximate useful ranges of four buffering systems selected for this study: succinic acid  $\text{pK}_{a1}$ /succinate, acetic acid/acetate, monobasic/dibasic phosphate, and dibasic/tribasic phosphate.

### Catalysts and Catalytic Controls

Aluminum sulfate, a.k.a. papermaker's alum (20 mM  $\text{Al}_2(\text{SO}_4)_3$ ) was the first salt studied in this project for its hypothesized role as a catalyst. In order to see the effects of the  $\text{Al}^{\text{III}}$  metal center, sulfate had to be present in the same amount in the control. Accordingly lanthanum sulfate was used, since the lanthanumIII cation ( $\text{La}^{\text{III}}$ ) is much larger and heavier than  $\text{Al}^{\text{III}}$ , thus not a candidate for electrophilic attack. The addition of this salt to the control series also controlled for the kinetic ionic strength effect, which is the phenomenon whereby reactions are observed to proceed faster with a higher overall concentration of salts (that do not necessarily participate in the degradation mechanism). While  $\text{Mg}^{\text{II}}$  opposite a number of anions is of continuing interest in this study given the many  $\text{Mg}^{\text{II}}$  compounds used over the years for aqueous and non-aqueous deacidification (Baty, Maitland et al. 2010), the first step was to study  $\text{Mg}^{\text{II}}$  opposite sulfate to draw the analogy from the aluminum/lanthanum series—isolating the effects of the cation. Still, this comparison cannot be a direct one because  $\text{Mg}^{\text{II}}$  is divalent and  $\text{Al}^{\text{III}}$ ,  $\text{La}^{\text{III}}$  are trivalent.

### Reaction Vessels

This section is expanded to present a case study of particular concern to conservation—reaction vessels for accelerated aging. Although there is no apparent consensus among conservation scientists on the preferred method of accelerated aging between humid oven and sealed vessel methods, for this study the sealed vessel approach, advocated for example by the Library of Congress (2009), was selected for two reasons: (1) An inert atmosphere can more easily be achieved in a sealed vessel. (Nitrogen gas was used to control for oxidative mechanisms

contributing to the degradation and skewing the results.) (2) A sealed vessel provides appropriate containment for the first phase of this work where the fibers were aged in excess water.

Selecting a sealed vessel approach, it was intended to follow the ASTM standard accelerated aging test method (2007) as closely as possible. It was especially intended to follow the specifications for the aging vessel, and products explicitly mentioned in the standard (section 6.4.1) were evaluated. The preliminary step of aging the paper fibers in excess water proved very revealing in this exercise, since it was noticed almost immediately that the aqueous phases were escaping from the vessels in a few hours at temperatures at or below the specified standard temperature ( $100 \pm 1.0^\circ\text{C}$ ). In the case of the products named in the standard, an explanation for the failures was found in fractures visible in the caps (fig. 4). Several other candidate vessels with various sealing mechanisms also failed, however, with no failure mode visible. It is therefore suspected that a number of previous sealed vessel aging studies may have been compromised by the escape of water vapor that was imperceptible to the investigator.



Fig. 4. Failed accelerated aging vessel showing fractures on the screw cap

Admittedly, a vessel with ample liquid water in it will have additional pressure (attributable to the saturated vapor pressure and the thermal expansion of the aqueous phase) than just water vapor or adsorbed water at the same temperature. Note however that (1) the saturated vapor pressure is not an overwhelming component of the total pressure at temperatures commonly used for accelerated aging, and (2) many vessels tested in this study failed at temperatures  $10\text{--}20^\circ\text{C}$  below the specified standard temperature ( $100^\circ\text{C}$ ).

To overcome this obstacle of failing aging vessels and to create a useful tool for conservation scientists and conservators, considerable effort was expended to develop an aging vessel testing procedure. The concept was to specify a volume of deionized water to put into vessels and to specify a temperature at which to heat the vessels overnight that will exert the same pressure on the vessels as the actual aging test will. No loss of the deionized water by the following day would establish the suitability of the vessel for the aging application. At press time the approach of basing the procedure on existing saturated vapor pressure equations has just been abandoned and the authors are now working on a procedure derived from empirically determined data specifically for this application.

A second concern for the sealed vessel aging study, voiced by the senior project conservator, was the possibility of off-gassing caused by plastic caps and seals. While the physical scientists on the team were not initially concerned about the use of solid fluoropolymer (e.g. Teflon) or fluoropolymer-lined caps or gaskets exposed to the headspace, that argument assumed that the fluoropolymer be of good quality and completely cover any other material of concern throughout the course of an experiment. Because the means of verifying that off-gassing was *not* occurring (e.g. solid phase microextraction/gas chromatography) was not readily accessible to this laboratory, nor is it accessible to most conservation and conservation science laboratories, considerable effort went into the development of a glass-on-glass seal for an accelerated aging vessel. Currently this vessel is in development but not yet incorporated into this study. Rather, two different vessels were selected following preliminary testing. For temperatures  $\leq 50^\circ\text{C}$ , glass bottles (100 mL, part number 21 801 24 09) and fluoropolymer-lined polybutylene terephthalate (PBT) screw caps (part number 29 240 28 07) were obtained from Schott North America Inc.; for temperatures above  $50^\circ\text{C}$ , Ace Glass Inc. pressure bottles (part number 8648-194 modified to have a flat bottom for a maceration surface), were used out of an abundance of caution. These were sealed with their fluoroelastomer-with-tetrafluoroethylene-additives (FETFE) O-Rings and solid polytetrafluoroethylene (PTFE) plugs (part number 5846-51).

#### *Reaction Vessel Loading and Maceration*

Whatman 42 paper was cut into chips (0.5–1.0 cm each dimension, as in TAPPI 2002), conditioned, and divided into aliquots ( $1 \pm 0.01$  g equivalent oven-dry weight). In a glove

bag, buffering solutions containing catalysts/catalytic controls and a specific make of stir bar (Fisherbrand octagonal 3/8 x 1 1/2 in., part number 14-513-52) were sparged (1 hr., UHP 99.999% grade N<sub>2</sub>) under a blanket of N<sub>2</sub> measuring  $\leq 0.5\%$  O<sub>2</sub>, the paper added and the vessels sealed. The paper was macerated by magnetic stirring (2 hrs.) on stir plates measuring 750 RPM under a standard condition. Each sample was rotated among all stir plates during the maceration to equally distribute any differences in mechanical action delivered by the different stir plates.

#### Incubation

Temperatures were controlled to within  $\pm 4^\circ\text{C}$  (Fisher Isotemp 725G, Lunaire Steady State Stability Test Chamber CEO910-3). Incubation temperatures and time are reported in the results section. Since the exposures are days to weeks in duration, warm-up time was negligible. After incubation, samples vessels were weighed to detect failures and cooled at  $4^\circ\text{C}$  prior to analysis.

#### Analysis

Each sample pH was determined to verify buffering during incubation, the fibers rinsed in DI H<sub>2</sub>O/EtOH (anhy.) with the filter cake collected from EtOH (Büchner filtration, 20–25  $\mu\text{m}$  pore size Whatman Quantitative Grade), which was dried ( $105^\circ\text{C}$ , 4 hrs.). Tricarbanilate derivatization was performed according to Stol, Pedersoli and co-workers (2002) as follows: Into a glass reaction vial, dry sample ( $5.0 \pm 0.2$  mg) was tweezed, 1.00 mL anhy. pyridine solvent, and 0.100 mL phenylisocyanate reactant added. After derivatization (48.0 hrs.,  $80 \pm 0.4^\circ\text{C}$ ), the reaction was stopped with 0.100 mL MeOH, the solution allowed to cool, and diluted with 2.03 mL tetrahydrofuran.

The solutions were filtered (0.20  $\mu\text{m}$ ) using a syringe-mounted filter and analyzed via Gel Permeation Chromatography–UV detection, using a Shimadzu Prominence GPC (LC-20AT pump, CBM-20Alite controller, SPD-20A UV detector). Separation in tetrahydrofuran of injection volume 40  $\mu\text{L}$  was achieved on one Waters Styragel HR 4 and one Waters Styragel HR 5 in series at  $35^\circ\text{C}$ , flow rate 0.500 mL/min, the system calibrated with polystyrenes. All samples, controls, and initial condition measurements were run in triplicate.

## RESULTS AND DISCUSSION

Figure 5 shows the useful ranges of the buffering salts given in figure 3, plotting the data sets obtained thus far at combinations of temperatures 40, 50, and  $90^\circ\text{C}$ ; and pH 3.3, 5.0, 6.9, and 8.2. To date, all results are from the first phase of the research, in which we aged the fibers in excess water. Aluminum sulfate, a.k.a. papermaker's alum, is currently the primary salt we are investigating for catalysis of degradation

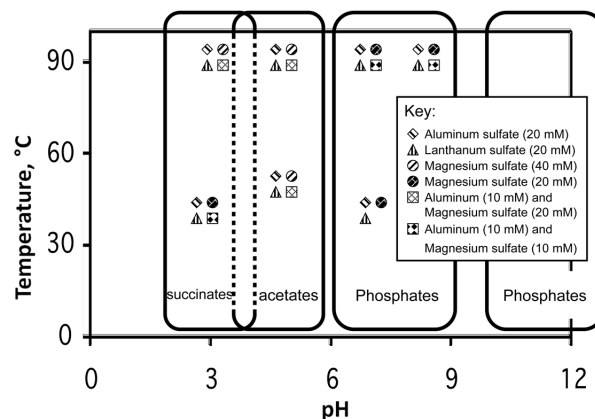


Fig. 5. Formulations (buffering systems, catalysts/catalytic controls, pH) and conditions (temperature) of data sets obtained

in this study, since it overtook potassium aluminum sulfate during the 19th century as the prevailing industrial aluminum salt (Brückle 1993). We selected the concentration (20 mM  $\text{Al}_2(\text{SO}_4)_3$ ) to draw the analogy between our results and those of the previous small molecule study (Baty and Sinnott 2004; 2005) in which the ratio of metal cations to cellulose monomers is the same. The concentration selected for this (and the previous) study we expect to conservatively underrepresent the  $\text{Al}^{\text{III}}$  concentration of, for example, 20th century publication papers: Priest, Stanley, and coworkers (1998) found a range of 1.3%–6.7%  $\text{Al}_2(\text{SO}_4)_3$  (average 3.8%) for such papers using atomic absorption spectroscopy of acid extracts. To observe the role of the  $\text{Al}^{\text{III}}$  ion while controlling for sulfate concentration and ionic strength, we set aluminum and lanthanum sulfate at a consistent concentration throughout the series, 20 mM with respect to the salt and 40 mM with respect to the cation. Two different concentrations of the magnesium sulfate (and the aluminum and magnesium salts together) represent a change in our thinking for the magnesium salt concentration. At first we held the overall salt concentration equal to the aluminum/lanthanum series. Later, since the objective was to test destabilization due to the cation ( $\text{Mg}^{\text{II}}$ ), we doubled the concentration to hold the cation concentration the same as those of the aluminum/lanthanum series. But note that this adjustment then makes the *sulfate* concentrations different.

Figures 6–9 show the weight average molecular weights of tricarbanilate-derivatized cellulose for the initial condition, samples, and controls. Since we calibrated the columns using polystyrene standards, the reported weights are offset by some as yet undetermined factor. While we are currently working to determine the absolute molecular weight using multiangle light scattering detection (MALS), for many useful kinetics criteria we do not need the absolute molecular weight. Moreover, we clearly see unambiguous effects of the catalyst relative to the initial condition and kinetic ionic strength effect controls in these results. Specifically, figures

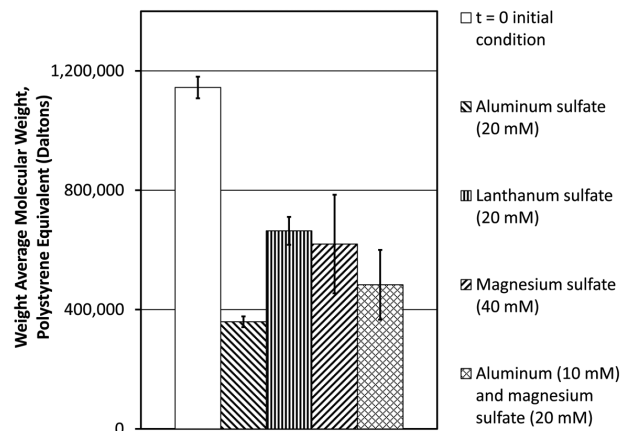


Fig. 6. Weight average molecular weight (derivatized cellulose) of samples exposed to pH 3.3 (succinates), 90°C, and 1.6 days, with catalysts and catalytic controls as labeled. Error bars are plus and minus one standard deviation

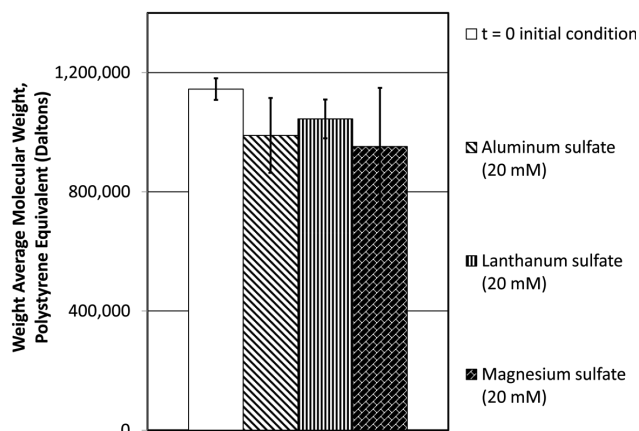


Fig. 9. Weight average molecular weight (derivatized cellulose) of samples exposed to pH 6.9 (monobasic/dibasic phosphate), 40°C, 29 days, with catalysts and catalytic controls as labeled. Error bars are plus and minus one standard deviation

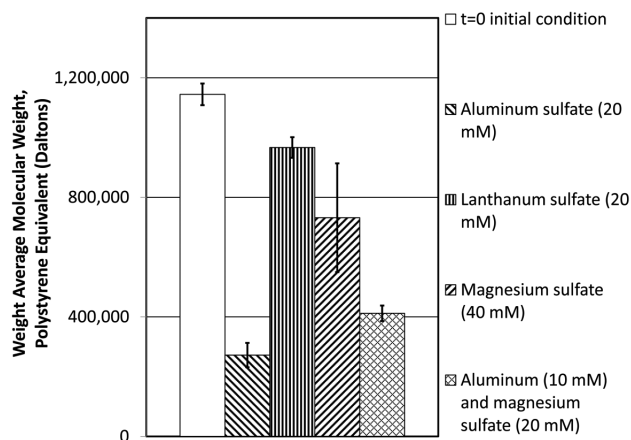


Fig. 7. Weight average molecular weight (derivatized cellulose) of samples exposed to pH 5.0 (acetates), 90°C, 8 days, with catalysts and catalytic controls as labeled. Error bars are plus and minus one standard deviation

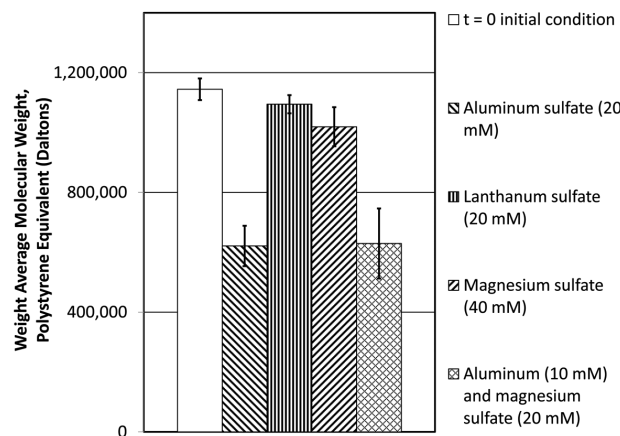


Fig. 8. Weight average molecular weight (derivatized cellulose) of samples exposed to pH 5.0 (acetates), 50°C, 8 days, with catalysts and catalytic controls as labeled. Error bars are plus and minus one standard deviation

6–8 show significant destabilization of the cellulose by the  $\text{Al}^{\text{III}}$  cation, controlling for (1) the pH, (2) the kinetic ionic strength effect, and (3) the anion identity—sulfate. The hypothesis that acidic papers degrade significantly via an  $\text{Al}^{\text{III}}$ -catalyzed route is therefore strongly supported here.

We expect the sulfate anion to influence the rate of degradation in this reaction, rendering the  $\text{Al}^{\text{III}}$  center less active than it would be opposite chloride, both of which Chamberlain (2007) has measured. This decreased activity may be due to anation of the  $\text{Al}^{\text{III}}$  by the sulfate (Baty and Sinnott 2005). Despite this likely reduction in rate caused by the anion, we still see unambiguous effects.

This effect of cellulose destabilization in the presence of  $\text{Al}^{\text{III}}$  is apparently pH dependant, however. Notice in figure 9, showing aging at pH 6.9, there is no significant difference between the  $\text{Al}^{\text{III}}$ -containing sample and controls, supporting the premise that neutralization via deacidification of these papers may be an effective means of limiting the  $\text{Al}^{\text{III}}$ -catalyzed mechanism of degradation, as it is for the proton-catalyzed route.

Similarly encouraging is the apparent benign behavior of  $\text{Mg}^{\text{II}}$ , which we tested here for its possible role as an electrophilic catalyst for hydrolysis. Throughout these tests, we observe no significant difference in degradation between the  $\text{Mg}^{\text{II}}$ -containing samples and the controls. While the data do not establish significance, the seemingly wider distribution of weight average molecular weights of the magnesium-containing sample sets relative to the  $\text{Al}^{\text{III}}$  and  $\text{La}^{\text{III}}$  samples seen in figures 6, 7, and 9 is worthy of further study. Some presently unseen variable may be at work slowing or promoting the mechanism under these conditions.

Finally, results from those samples containing both  $\text{Al}^{\text{III}}$  and  $\text{Mg}^{\text{II}}$  together (figs. 6–8) offer no surprising results. We added both of these two metal cations to samples to see

whether acting together they will increase or decrease catalytic activity, a phenomenon that Shahani, Hengemihle, and Kresh (1995) observed previously in the oxidative degradation of paper-based heritage collections. This phenomenon is especially pertinent to  $\text{Al}^{\text{III}}$ , which will readily form polynuclear coordination complexes under certain conditions in aqueous environments. The degradation we observe to date, however, may be approximately that which we would expect from the suspected catalysts acting independently with no “sympathetic” effect in evidence.

## CONCLUSIONS

1. We observe significant loss of cellulose degree of polymerization of paper fibers due to the presence of  $\text{Al}^{\text{III}}$  at pH 3.3 and 5.0, while controlling for critical variables including:

A. pH

B. Ionic strength

C. Counterion identity—sulfate

This result strongly supports the hypothesis that cellulose hydrolysis proceeds substantially via a different chemical mechanism in  $\text{Al}^{\text{III}}$ -containing papers than the proton-catalyzed mechanism conservation scientists previously believed to be the primary cause of this degradation.

2. Preliminary pH dependence results suggest that, as pH reaches 6.9, destabilization by  $\text{Al}^{\text{III}}$  is no longer active, supporting the hypothesis that deacidification is an effective means of stopping the electrophile-catalyzed hydrolysis.
3. Because, like  $\text{Al}^{\text{III}}$ ,  $\text{Mg}^{\text{II}}$  is also electrophilic, we tested it for its ability to catalyze cellulose hydrolysis. Under the conditions of this experiment, however, we did not observe destabilization by  $\text{Mg}^{\text{II}}$ , revealing no evidence of new concerns for its use in a deacidification agent.

## FUTURE WORK

This research agenda will continue through summer 2011, during which time we will carry out the evaluation of pH dependence of the  $\text{Al}^{\text{III}}$ -catalyzed cellulose hydrolysis in conditions relevant to paper-based heritage collections, since this dependence appears to be discontinuous. As presented above, preliminary data suggest that this mechanism is highly significant at pH 5.0 and below—but not observed at pH 6.9—suggesting that deacidification should be an effective means of conserving papers containing  $\text{Al}^{\text{III}}$ . It is important to determine, however, that there are not any “hot spots”—meaning pH ranges or other factors at which increased catalytic activity is observed—the knowledge of which could aid in deacidification strategy. We will also continue to study two metal centers present together in the paper, particularly the combination of  $\text{Al}^{\text{III}}$  and  $\text{Mg}^{\text{II}}$  for its relevance to deacidification.

Reinforced by the pH dependence data, we will acquire additional temperature dependence data for the  $\text{Al}^{\text{III}}$ -catalyzed mechanism, from which the important criterion of activation energy is soluble. This criterion is needed to forecast the significance of the mechanism to ambient (library/museum/archival) conditions. Also, since the mechanism clearly works in combination with the proton-catalyzed path, activation energy is needed to gauge its contribution to overall degradation at different conditions.

Finally, we will extend the experimental design set up for this work to the study of other metal centers that have the potential to be catalysts for hydrolysis or oxidation. Since we have taken particular care in this method to limit oxidation (and to control proton-catalyzed hydrolysis using common-effect buffers) this is a unique opportunity to see how these mechanisms “fit together” to work the degradation in paper-based heritage collections.

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## REFERENCES

- AIC 2010 Posters 3. 2010. American Institute for Conservation of Historic and Artistic Works. Washington, DC. [www.conservation-us.org/index.cfm?fuseaction=page.viewpage&pageid=1261#25](http://www.conservation-us.org/index.cfm?fuseaction=page.viewpage&pageid=1261#25) (accessed 07/14/10).
- ASTM. 2007. Standard test method for accelerated temperature aging of printing and writing paper by dry oven exposure apparatus, D6819-02. West Conshohocken, Pa.: American Society for Testing and Materials International.
- Barański, A., R. Dziembaj, A. Konieczna-Molenda, J. M. Łagan, and S. Walas. 2004. On the applicability of [the] Arrhenius equation to accelerated ageing tests: The case of alum-impregnated cellulose. *Polish Journal of Chemical Technology* 6(1): 1–8.
- Baty, J., and M. L. Sinnott. 2004. Efficient electrophilic catalysis of 1,5-anhydrocellobiitol hydrolysis by  $\text{Al}^{\text{III}}$ ; Implications for the conservation of “rosin-alum” sized paper. *Chemical Communications* 7: 866–7.

- Baty, J., C. L. Maitland, W. Minter, M. A. Hubbe, and S. K. Jordan-Mowery. 2010. Deacidification for the conservation and preservation of paper-based works: A review. *BioResources* 5(3): 1955–2023 [Online]. <http://www.ncsu.edu/bioresources/> (accessed 07/20/10).
- Baty, J. W., and M. L. Sinnott, M. L. 2005. The kinetics of the spontaneous, proton- and Al<sup>III</sup>- catalysed hydrolysis of 1,5-anhydrocellobiitol—Models for cellulose depolymerization in paper aging and alkaline pulping, and a benchmark for cellulase efficiency. *Canadian Journal of Chemistry* 83: 1516–24.
- Brückle, I. The role of alum in historical papermaking. 1993. *Abbey Newsletter* 17(4) [Online]. <http://palimpsest.stanford.edu/byorg/abbey/an/an17/an17-4/an17-407.html> (accessed 07/14/10).
- Chamberlain, D. Anion mediation of aluminium-catalysed degradation of paper. 2007. *Polymer Degradation and Stability* 92: 1417–20.
- Clark, C. R., and R. W. Hay. 1973. Acid-catalysed and metal-ion-catalyzed hydrolysis of 8-quinolyl β-D-glucopyranoside. *Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry* 14: 1943–7.
- Clark, C. R., R. W. Hay, and I. C. M. Dea. 1970. Metal-ion catalyzed glucoside hydrolysis. *Journal of the Chemical Society [Section] D: Chemical Communications* 13: 794–5.
- Dawson, R. M. C., D. C. Elliott, W. H. Elliott, and K. M. Jones. 1986. *Data for biochemical research*. Oxford: Oxford University Press.
- Gurnagul, N., R. C. Howard, X. Zou, T. Uesaka, and D. H. Page. 1993. The mechanical permanence of paper: A literature review. *Journal of Pulp and Paper Science* 19(4): J160–6.
- HSC Participation at the AIC 2010 Conference. 2010. Heritage Science for Conservation, Department of Conservation and Preservation-The Sheridan Libraries. Johns Hopkins University, Baltimore. [www.library.jhu.edu/departments/preservation/hcs/aic](http://www.library.jhu.edu/departments/preservation/hcs/aic) (accessed 07/14/10).
- Library of Congress Preservation Directorate. 2009. Improved traditional paper accelerated aging tests. Library of Congress, Washington, DC. [www.loc.gov/preserv/rt/projects/acc\\_aging\\_test.html](http://www.loc.gov/preserv/rt/projects/acc_aging_test.html) (accessed 07/19/10).
- Parks, E. J. 1971. Thermal analysis of modified cellulose. *Tappi* 54(4): 537–44.
- Popoola, A. V. 1991. Acid hydrolysis of cotton. *Cellulose Chemistry and Technology* 25: 19–21.
- Priest, D. J., and M. Farrar. 1994. The effect of aluminium salts on the degradation of paper. *Proceedings of Symposium* 88. Ottawa, Canada. 255–62.
- Priest, D. J., J. Stanley, and A. Karademir. 1998. Characteristics of twentieth-century lignin-containing publication papers. *IPC Conference Papers*. London. 291–6.
- Scott, W. E. 1996. *Principles of Wet End Chemistry*. Atlanta: Tappi Press.
- Shahani, C. J., F. H. Hengemihle, and D. Kresh. 1995. Effect of some deacidification agents on copper-catalyzed degradation of paper—Preservation research and testing series No. 9501. Library of Congress, Washington, DC. [www.loc.gov/preserv/rt/copper/cops.html](http://www.loc.gov/preserv/rt/copper/cops.html) (accessed 07/20/10).
- Stanley, J. 1992. The ageing and deterioration of papers made with modern pulps. Ph.D. thesis, The Victoria University of Manchester, Manchester, UK.
- Stol, R., J. L. Pedersoli Jr., H. Poppe, and W. Th. Kok. 2002. Application of size exclusion electrochromatography to the microanalytical determination of the molecular mass distribution of celluloses from objects of cultural and historical value. *Analytical Chemistry* 74: 2314–20.
- TAPPI. 1998. Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products, T 402 sp-98. Atlanta: Technical Association of the Pulp and Paper Industry.
- TAPPI. 2002. Hydrogen ion concentration (pH) of paper extracts (hot extraction method), T 435 om-02. Atlanta: Technical Association of the Pulp and Paper Industry.
- W. J. Barrow Research Laboratory Inc. 1974. *Permanence/durability of the book*, Vol. 7, *Physical and chemical properties of book papers 1507–1949*. Richmond, Virginia: W. J. Barrow Research Laboratory Inc.

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