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To cite this article: Piero Baglioni, David Chelazzi, Rodorico Giorgi & Giovanna Poggi (25 Sep 2023): A Reply to 'A Note of Caution on the Use of Calcium Nanoparticle Dispersions as Deacidifying Agents', *Studies in Conservation*, DOI: [10.1080/00393630.2023.2260631](https://doi.org/10.1080/00393630.2023.2260631)

To link to this article: <https://doi.org/10.1080/00393630.2023.2260631>



Published online: 25 Sep 2023.



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A Reply to 'A Note of Caution on the Use of Calcium Nanoparticle Dispersions as Deacidifying Agents'

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ABSTRACT

The application of $\text{Ca}(\text{OH})_2$ nanoparticles dispersed in short chain alcohols to adjust the pH of acidic cellulosic substrates (paper, canvas, and wood) has been introduced and largely assessed in conservation practice, and commercial products are available on the market. Recently, some concerns about this methodology were expressed in a technical note ('A Note of Caution on the Use of Calcium Nanoparticle Dispersions as Deacidifying Agents' by Cremonesi (2023)). The main criticism is that carbonation of the hydroxide particles into calcium carbonate could be too slow, and the $\text{Ca}(\text{OH})_2$ remaining on the fibers might cause structural damage to cellulose by producing high alkalinity *in situ*, when water absorbed by the alcohol dispersion or by the cellulose-based support causes dissociation in the nanoparticles. However, in Cremonesi's note, no accurate description of the application method was given, and some fundamental information already present in the literature was overlooked. Here, we give a rebuttal of Cremonesi's conclusions, providing: (1) further evidence that the correct application of the particles' dispersions results in carbonation and in neutral pH values in a few days; and (2) an up-to-date literature survey, in which the $\text{Ca}(\text{OH})_2$ nanoparticles' carbonation kinetics is studied in detail, and potential structural damage to cellulosic materials in an alkaline environment is evaluated and ruled out.

ARTICLE HISTORY

Received February 2023
Accepted September 2023

KEYWORDS

Deacidification; pH adjustment; paper restoration; calcium hydroxide nanoparticles

Introduction

Deacidification, or pH adjustment, is one of the major measures taken in the remedial conservation of paper artifacts in archives, collections, museums, and libraries (Baty et al. 2010; Horst et al. 2020; Zervos and Alexopoulou 2015); in addition, specific and advanced methodologies, including nanotechnologies, have been proposed over the years for cellulosic substrates (Amornkitbamrung et al. 2020; Giorgi et al. 2002; Giorgi et al. 2002; Giorgi et al. 2009; Giorgi, Bozzi, et al. 2005; Lunjakorn et al. 2018; Palladino et al. 2020; Poggi et al. 2010; Xu et al. 2020) (paper, canvas, wood) and for collagen-based objects (Baglioni et al. 2016; Bartoletti, Odlyha, and Bozec 2022) (parchment, leather). In the last decades, both aqueous and non-aqueous deacidification methods have been adopted in conservation practice and reviewed in the literature, including the use of micro- and nanoparticles (e.g. oxides or hydroxides of alkaline earth metals) dispersed in organic solvents, which are available on the market and are currently employed in mass treatments or in the restoration of single items (Baty et al. 2010; Zumbühl and Wulfert 2001; Buchanan et al. 2022). In principle, because artifacts and their components (inks, dyes, etc.) can in some cases exhibit fragility or sensitivity to some chemicals, solvents and specific application procedures, it is

fundamental to provide protocols to guide end-users as much as possible in the utilization of advanced and functional materials, such as those formulated in the framework of colloids and material science.

Recently, our attention was caught by a technical note in *Studies in Conservation*, 'A Note of Caution on the Use of Calcium Nanoparticle Dispersions as Deacidifying Agents', by Cremonesi (2023), in which some conclusions and recommendations were provided that highlight a potential risk associated with the use of calcium hydroxide nano-dispersions (Giorgi, Chelazzi, and Baglioni 2005; Poggi et al. 2014; Poggi, Toccafondi, et al. 2016) for the deacidification of cellulosic supports. In particular the note refers to the formulations commercially available under the name Nanorestore Paper[®], which comprises $\text{Ca}(\text{OH})_2$ nanoparticles dispersed either in ethanol or 2-propanol, with concentrations of 3 or 5 g/L. The note expresses one main concern: that, after treatment, the transformation of $\text{Ca}(\text{OH})_2$ nanoparticles into the milder alkali CaCO_3 by reaction with atmospheric CO_2 (carbonation reaction) might take too long (weeks or even months), resulting in the prolonged presence of calcium hydroxide on the cellulosic fibers. This, as advised in the note, would potentially expose cellulosic materials to structural damage owing to the highly alkaline aqueous environment formed *in situ* when water absorbed by

the alcohol dispersion or by the cellulose-based support causes hydroxide dissociation in the $\text{Ca}(\text{OH})_2$ nanoparticles. However, after carefully examining the article, we found that the criticisms and caution notes therein contained are based on incorrect procedures and overlook some fundamental information contained in the literature on these topics, thus leading to wrong assumptions. In particular, we found that two aspects make the note inaccurate and misleading. First, no detailed description is given as of how the nanoparticles' dispersions were applied onto the samples, e.g. in terms of quantity or application procedure, simply stating that 'The application was done following the recommendations of the Nanorestore™ technical data sheet'; we will demonstrate here that following the product's technical data sheet requires much shorter carbonation times than those included in the note. Second, Cremonesi only presents part of the literature on the topics of the effects of alkalinity on the cellulose fibers, and of the carbonation mechanism of calcium hydroxide nanoparticles, overlooking significant contributions of carbonation kinetic studies, or reports that evaluated and excluded potential damage induced on cellulose by an alkaline environment.

As the original developers of Nanorestore Paper® formulations, and based on our past and current understanding of these systems, we are thus providing here a rebuttal of the conclusions contained in Cremonesi's technical note (2023), bringing further evidence on the systems, and an up-to-date survey of the scientific literature on the effect of an alkaline environment on paper permanence.

Materials and methods

Materials

Two types of cellulose-based paper have been selected for the present study: (1) filter paper (qualitative grade from cotton linters, paper grammage 75 g/m^2 , Munktell, pH 6.5), representative of a system that does not need to be deacidified, but only protected with the deposition of a buffer. This sample is labeled as FT; (2) acidic paper (paper grammage 90 g/cm^2 , pH 4.5). This paper is composed of 70% hardwood bleached pulp, 30% softwood bleached pulp, and 20% pulp-filling agent kaolin OT80. Acidity is due to the presence of an acidic resinous sizing (Sacocell 309 aluminum sulphate). This sample, labeled as AP, is representative of acidic paper, in need of a deacidification treatment.

Application of $\text{Ca}(\text{OH})_2$ nanoparticles

FT mockups (about 80 cm^2) were treated with a total amount of 0.33 mL of calcium hydroxide nanoparticles dispersion in ethanol at a concentration of 3 g/L; AP

mockups (about 80 cm^2) were treated with a total amount of 3 mL of calcium hydroxide nanoparticles dispersion in ethanol at a concentration of 3 g/L. The dispersion was sprayed on both sides of samples using an airbrush (nozzle diameter 0.3 mm), connected to a compressor, set at 1 bar. During the application, the distance between the sample (mounted on a vertical support) and the airbrush was about 15 cm. For AP multiple applications ($250 \mu\text{L}$ each per side) were carried out until the chosen amount of dispersion was delivered. Between each application, the sample was let dry under the hood for a few minutes at 23°C and 50% RH. Samples were then placed in sealed containers and kept at 50% or at 75% RH for two weeks at 23°C , to allow the full conversion of calcium hydroxide excess into carbonate. The application protocol and the AP samples are representative of practical applications in paper conservation, while filter paper was here considered because it is commonly used as a reference material.

pH measurements

The pH of paper was measured using the following protocol: 70 mg of sample was weighed, cut in small pieces, and placed inside screw top vials. 5 mL of distilled water was added inside each vial, subsequently sealed to avoid the solubilization of CO_2 from air into water. Vials were kept under stirring for one hour before measuring the pH of the extraction by using a digital pH-meter (CrisonBasic 20, equipped with a combined electrode, model 52–21). The error associated to pH measurements on these samples is ± 0.2 . Although it is a destructive technique, we selected this methodology since it is significantly more accurate than pH indicators, such as phenophtalein or indicator paper.

Colorimetric measurements

A X-RITE SP60 VIS portable spectrophotometer, with an integrating sphere having a circular sampling spot (diameter = 1.5 cm) was used to analyze the samples before and after deacidification. Colorimetric coordinates were obtained using standard illuminant D65 and a standard observer at 10° (CIE 1964). The color difference between samples can be expressed in terms of the ΔE^* parameter, calculated from the colorimetric coordinates L^* , a^* , and b^* , following the CIEDE2000 definition (Sharma, Wu, and Dalal 2005). The experimental error on ΔE^* is about ± 0.75 .

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra in ATR (attenuated total reflection) mode were carried out on the paper samples, before and after treatment with the $\text{Ca}(\text{OH})_2$ nanoparticles. Measurements were taken exactly on the same spot

for each sample with a Cary 620–670 FTIR microscope (Agilent Technologies), using a single element MCT detector and an ATR slide with a Ge crystal mounted on the 15x Cassegrain objective; 128 scans were acquired for each spectrum in the 3900–650 cm^{-1} spectral range using an open aperture and a spectral resolution of 4 cm^{-1} .

Results and discussion

Experimental results

The first fundamental point in our rebuttal of the conclusions contained in Cremonesi's technical note is that no accurate description was given as of how the nanoparticles' dispersions were applied onto the paper samples, simply stating that 'the application was done following the recommendations of the Nanorestore™ technical data sheet' (Cremonesi 2023). The product technical data sheet is based on published literature that describes the quantity of product applied, and the application procedure (Baglioni, Chelazzi, and Giorgi 2015) used for selected case studies. It is important to note that the calculation of the precise amount of nanoparticles needed to deacidify a substrate is not feasible in many practical cases, because several parameters, including starting pH, paper grammage, substrate porosity and the applicative procedure (i.e. immersion, spraying, dropping) should be considered. This accounts for variability in amounts applied in the literature. Nevertheless, the Nanorestore Paper® technical sheet (Nanorestore Paper Technical Data Sheet 2016) suggests the following quantities for the sole neutralization of acidity in paper samples: 1L of dispersion at 3 g/L can be used for the neutralization of 24 m^2 having a starting pH of 5 and a grammage of 80 g/m^2 ; 1L of dispersion at 3 g/L can be used for the neutralization of 16 m^2 having a starting pH of 4 and a grammage of 100 g/m^2 . In addition, if the formation of an alkaline reserve is desired, higher amounts of dispersions (2–3 times the initial application) should be applied after neutralization, as reported in the technical sheet.

Using these indications as guidelines, we treated here two different types of paper (FT and AP) as detailed in the *Materials and Methods* section, which were then let dry and rest in containers at 23°C and 50% or 75% RH. The first RH value was selected as representative of dry, controlled, environments; the second RH value was chosen to reproduce the 70–80% RH reported in Cremonesi's note for this application. The Nanorestore Paper® technical sheet (Nanorestore Paper Technical Data Sheet) specifies that 'after the application of Nanorestore Paper® dispersions, it is advisable to keep treated artifacts at about 60% RH and room temperature for 10–15 days, in order to favor the conversion of calcium hydroxide to

carbonate'. It is worth noting that RH can be controlled using either saturated salt solutions (Young 1967) or water/glycerol solutions (Forney and Brandl 1992), which can be easily used in small laboratories or conservation ateliers. Colorimetric coordinates were acquired before and after treatment, to check for changes in the visual aspect of the samples. In addition, after 14 days, the pH of samples was measured. Finally, we studied the surface of the treated paper samples with ATR-FTIR after 7 and 14 days.

The experimental evidence we collected is as follows: (1) no changes have been detected on the colorimetric coordinates of the samples, i.e. the measured ΔE^* were lower than 1, which is close to the experimental error (± 0.75) and is significantly below the difference that can be perceived by the naked eye (Witzel, Burnham, and Onley 1973). (2) After 14 days, all samples display a pH around 6.5, independently from the RH of the climate chamber used. (3) In agreement with the pH measurements, the diagnostic IR peak of $\text{Ca}(\text{OH})_2$ ($-\text{OH}$ stretching band at 3650 cm^{-1}) disappeared completely after one week for FT samples (Figure 1(A,B)) and two weeks for AP samples (Figure 1(C,D)). This indicates that the $\text{Ca}(\text{OH})_2$ content is below the FTIR-ATR detection limit. It must be noticed that in the same IR region, AP samples display two signals that are due to kaolinite, i.e. the paper's filler, at 3695 cm^{-1} (stretching of $-\text{OH}$ groups reside at the octahedral surface) and 3620 cm^{-1} (stretching of inner $-\text{OH}$ groups lying between the tetrahedral and octahedral sheets) (Madejová 2003; Tironi et al. 2012). Therefore, a dashed line indicating the $\text{Ca}(\text{OH})_2$ peak in the AP spectra was added in the inset of Figure 1(C,D).

In some cases, the spectra of the treated samples show a weak absorption near 1600 cm^{-1} , ascribable to the salification of carboxyl groups in cellulose (Smith 2018; Zhabankov 1995), which were present in the pristine samples as evidenced by weak absorptions in the 1730–1700 cm^{-1} spectral range.

Overall, the dramatic reduction in hydroxyls' absorptions indicate that, when the particles are applied following the published guidelines and data sheets, carbonation takes place completely in the reported time span. Any possible hydroxide residue below the FTIR-ATR detection limit did not produce alkaline pH values on the treated paper, as confirmed by the pH measurements. This evidence has even more statistical relevance since much larger portions of papers are probed in the pH measurements than in the ATR spot size/volume.

This direct evidence was expected as the safe application and conservation efficacy of the $\text{Ca}(\text{OH})_2$ nanoparticles on different types of substrates (paper, canvas, wood) is well known in the literature spanning over two decades (Baglioni et al. 2013; Chelazzi, Giorgi, and Baglioni 2006; Giorgi, Chelazzi, and Baglioni 2005;

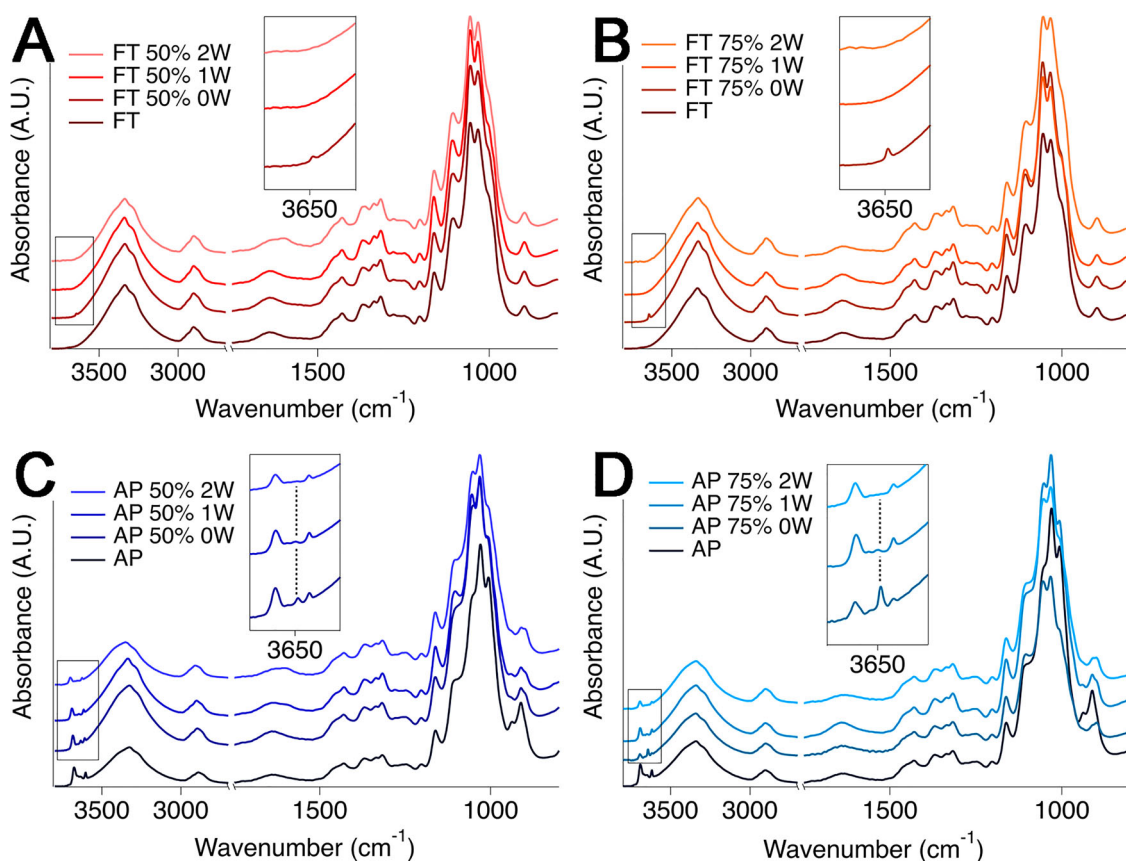


Figure 1. ATR-FTIR spectra of FT before and after one week and two weeks at 50% RH (A) or 75% RH (B). ATR-FTIR spectra of AP before and after one week and two weeks at 50% RH (C) or 75% RH (D). In the insets, the IR region around the diagnostic peak of $\text{Ca}(\text{OH})_2$ is shown. In (C) and (D), a dashed line was added to highlight the peak due to calcium hydroxide which is close to those of kaolinite at 3695 and 3620 cm^{-1} . The heterogeneity of samples is reasonably responsible for small changes in the peak intensity of calcium hydroxide and kaolinite of samples of the same series. Spectra are arbitrarily offset, for sake of clarity.

Nourinaeini et al. 2020; Poggi et al. 2014; Poggi et al. 2016; Poggi et al. 2016; Poggi et al. 2017; Poggi et al. 2020; Poggi, Baglioni, and Giorgi 2011).

As the developers of these formulations, we extensively assessed the systems in several case studies, discussing and publishing fundamental physico-chemical aspects (e.g. kinetics of calcium carbonate formation by the calcium hydroxide nanoparticles reacting with atmospheric CO_2 (Camerini et al. 2019) as well as practical applications (use of the formulations on paper, canvas, and other artistic/historical substrates). In these studies we showed that the systems are safe and beneficial in paper pH-adjustment as they increase paper permanence without affecting the degree of polymerization of cellulose (Nourinaeini et al. 2020; Poggi et al. 2014; Poggi et al. 2017; Poggi et al. 2020; Poggi, Baglioni, and Giorgi 2011), e.g. the cellulose DP of acidic paper remained the same before (551 ± 25) and after treatment (537 ± 25), prior to artificial aging (Nourinaeini et al. 2020; Poggi et al. 2020).

Literature survey on carbonation kinetics

Regarding the carbonation kinetics, Rodriguez-Navarro, Elert, and Ševčík (2016) monitored the

formation of amorphous and crystalline calcium carbonate from commercial $\text{Ca}(\text{OH})_2$ nanoparticles (Calosil®). The process kinetics were fitted to a solid-state deceleratory kinetic model that had been previously reviewed by Khawam and Flanagan (2006). Afterwards, we investigated the behavior of different formulations of nanoparticles (Camerini et al. 2019), adopting the mathematical 'Boundary Nucleation and Growth' model (BNGM) originally developed by Cahn (1956) and further implemented by Thomas (2007) to describe the hydration of tricalcium silicate. Namely, we used the BNGM to study the influence of the liquid medium (ethanol, 2-propanol) and particles' specific surface area on the carbonation kinetics and activation energies. The quantity of particles deposited per unit area in the kinetic study (Camerini et al. 2019) was 1–2 orders of magnitude higher than what is recommended in the protocols and technical sheet for the neutralization of paper, thus it represents a pessimistic scenario with respect to the applications reported in the present contribution, which follows the paper protocols. In the carbonation kinetic study, the particles were let react with atmospheric CO_2 (450 ppm) at 75% RH and different temperatures (14°C, 22°C, and 30°C), following quantitatively the transformation of

Ca(OH)₂ into CaCO₃ via FTIR. The results showed that complete transformation of Ca(OH)₂ into CaCO₃ at 22°C took place within 4–8 h from application for all the nanoparticles with size of 50–250 nm (hexagonal platelets) and specific surface area of 36–38 m²g⁻¹, which are representative of the Nanorestore Paper® products for paper deacidification and of Calosil® (Camerini et al. 2019). In the case of larger particles (300–500 nm, with few micron-sized aggregates) with surface area of 20 m²g⁻¹, the time required for full carbonation at room T and 75% RH was ca. 20 h. The presence of different substrates and different mobility of the chemical species involved in the carbonation process likely explain the different carbonation rates. The carbonation process is even faster for increasing RH values, even though the stable presence of bulk water in contact with the particles' surface can inhibit the reaction since water is one of the products. The evidence of slow carbonation of lime in murals, brought on by Cremonesi (2023), cannot be compared to the application (and carbonation) of microfilms of Ca(OH)₂ nanoparticles on the surface of paper. Such a simple, direct comparison overlooks fundamental concepts of surface chemistry and physics, e.g. different specific surface area of the lime grains and nanoparticles, different accessibility of CO₂ to the boundaries of lime grains in murals and particles in surface microfilms, and different surface concentration of lime grains in murals and particles on the surface of paper.

Literature survey on the effect of alkalinity on paper permanence

One of the main concerns reported in Cremonesi's article is that an alkaline environment after a deacidification treatment could be detrimental for paper and/or canvas (Cremonesi 2023). When the particles are applied following the Nanorestore Paper® technical sheet (Nanorestore Paper Technical Data Sheet 2016), a pH of about 7–8 should be measured. As reported in the technical sheet (Nanorestore Paper Technical Data Sheet 2016), 'A deacidification treatment is needed when the measured pH is lower than 5.5'. In any case, fundamental studies, such as those by Ahn et al. clearly demonstrate that deacidification treatments of real paper samples produce beneficial effects that outweigh any possible damage coming from the deposited alkaline reserve (Ahn et al. 2012; Ahn, Rosenau, and Potthast 2013). In detail, GPC analysis and determination of carbonyl functionalities were performed on samples following treatment with different deacidification methods and aging. Surface pH values as high as 9.3 were reached upon deacidification. The main concern was on the possibility of β-alkoxy elimination taking place when oxidized paper, such as old manuscripts, is put in contact with chemicals at high pH values. This reaction starts with the attack by an alkali to a hydrogen atom in

position α with respect to a carbonyl group and leads to the elimination of the whole group in position β. In principle, at pH higher than 10, an isomerization of the reducing end in cellulose chains results in the migration of the carbonyl group, and β-alkoxy elimination can thus cause random cleavage of the cellulose chain, leading to macroscopic degradation. In practice, however, Ahn et al. established that the risk of chain scission by β-elimination in naturally oxidized cellulose as a consequence of deacidification is not significant, owing to the characteristic distribution of carbonyl groups in cellulose in naturally-aged papers (Ahn et al. 2012; Ahn, Rosenau, and Potthast 2013). Following further detailed chemical analysis, the authors concluded that, although some indication of β-elimination was found on the alkali-treated paper items, the reaction did not occur to an extent that significantly influenced the molar mass of cellulose (Ahn et al. 2012; Ahn, Rosenau, and Potthast 2013). The authors thus evaluated that the beneficial effect of alkali reserve, i.e. decreasing the rate of acid-catalyzed hydrolytic degradation in acidic paper, clearly outweighed possible negative alkalinity effects due to the deposited alkaline reserve (Ahn et al. 2012; Ahn, Rosenau, and Potthast 2013). This evidence provided by independent experts is in line with our conclusions based on viscosimetric DP measurements carried out on deacidified paper samples, even subjected to strong aging conditions (Nourinaeini et al. 2020; Poggi et al. 2014; Poggi et al. 2017; Poggi et al. 2020; Poggi, Baglioni, and Giorgi 2011). Such experimental proof was completely overlooked in Cremonesi's note.

For what concerns paper additives and media, such as inks and dyes, their sensitiveness to the alkalis and solvents used for deacidification must be carefully checked before carrying out the treatment. As indicated in the Nanorestore Paper® technical sheet (Nanorestore Paper Technical Data Sheet 2016), 'Before the application of Nanorestore Paper® dispersions, the compatibility between the artifacts and the system should be checked.'

Thus, considering the additional evidence provided here about the conversion of Ca(OH)₂ nanoparticles and the up-to-date survey of the scientific literature on the effect of an alkaline environment on paper permanence, we firmly rebut the conclusions of Cremonesi's technical note (2023).

Conclusions

We demonstrated that, following the recommendations reported in published protocols and the technical data sheet, the application of Nanorestore Paper® results in the carbonation of calcium hydroxide nanoparticles and a pH close to neutrality within two weeks at room temperature and RH of 50% or 75%. No colorimetric alterations occurred to the treated paper samples. In addition, we provided an up-to-

date literature survey, comprising the work of different research groups, showing that an alkaline environment, even when pH is around 9, produces beneficial effects on paper artifacts that outweigh any possible chemical damage from alkalinity. Therefore, we conclude that Cremonesi's note is based on a limited knowledge of the systems under criticism, and we firmly rebut the conclusions therein reported.

Acknowledgements

The Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, CSGI (Center for Colloid and Surface Science) is gratefully acknowledged for financial support.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by CSGI.

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References

- Ahn, K., U. Henniges, G. Banik, and A. Potthast. 2012. "Is Cellulose Degradation Due to β -Elimination Processes a Threat in Mass Deacidification of Library Books?" *Cellulose* 19 (4): 1149–1159. <https://doi.org/10.1007/s10570-012-9723-3>.
- Ahn, K., T. Rosenau, and A. Potthast. 2013. "The Influence of Alkaline Reserve on the Aging Behavior of Book Papers." *Cellulose* 20 (4): 1989–2001. <https://doi.org/10.1007/s10570-013-9978-3>.
- Amornkitbamrung, L., D. Bračić, M. Bračić, S. Hribernik, J. Malešič, U. Hirn, A. Vesel, K. S. Kleinschek, R. Kargl, and T. Mohan. 2020. "Comparison of Trimethylsilyl Cellulose-stabilized Carbonate and Hydroxide Nanoparticles for Deacidification and Strengthening of Cellulose-Based Cultural Heritage." *ACS Omega* 5 (45): 29243–29256. <https://doi.org/10.1021/acsomega.0c03997>.
- Baglioni, M., A. Bartoletti, L. Bozec, D. Chelazzi, R. Giorgi, M. Odlyha, D. Pianorsi, G. Poggi, and P. Baglioni. 2016. "Nanomaterials for the Cleaning and PH Adjustment of Vegetable-tanned Leather." *Applied Physics A* 122 (2): 114. <https://doi.org/10.1007/s00339-015-9553-x>.
- Baglioni, P., D. Chelazzi, and R. Giorgi. 2015. *Nanotechnologies in the Conservation of Cultural Heritage – a Compendium of Materials and Techniques*. Heidelberg: Springer.
- Baglioni, P., D. Chelazzi, R. Giorgi, and G. Poggi. 2013. "Colloid and Materials Science for the Conservation of Cultural Heritage: Cleaning, Consolidation, and Deacidification." *Langmuir* 29 (17): 5110–5122. <https://doi.org/10.1021/la304456n>.
- Bartoletti, A., M. Odlyha, and L. Bozec. 2022. "Insights from the NANOforArt Project: Application of Calcium-based Nanoparticle Dispersions for Improved Preservation of Parchment Documents." *Restaurator. International Journal for the Preservation of Library and Archival Material* 43 (1–2): 143–158. <https://doi.org/10.1515/res-2022-0005>.
- Baty, J. W., 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: 1955–2023. <https://doi.org/10.15376/biores.5.3.1955-2023>.
- Buchanan, S., W. Bennett, M. Domach, S. Melnick, C. Tancin, and P. Whitmore. 2022. *An Evaluation of the Bookkeeper Mass Deacidification Process: Technical Evaluation Team Report for the Preservation Directorate, Library of Congress*. <http://www.loc.gov/preserv/deacid/bkkphome.html>.
- Cahn, J. W. 1956. "The Kinetics of Grain Boundary Nucleated Reactions." *Acta Metallurgica* 4 (5): 449–459. [https://doi.org/10.1016/0001-6160\(56\)90041-4](https://doi.org/10.1016/0001-6160(56)90041-4).
- Camerini, R., G. Poggi, D. Chelazzi, F. Ridi, R. Giorgi, and P. Baglioni. 2019. "The Carbonation Kinetics of Calcium Hydroxide Nanoparticles: A Boundary Nucleation and Growth Description." *Journal of Colloid and Interface Science* 547: 370–381. <https://doi.org/10.1016/j.jcis.2019.03.089>.
- Chelazzi, D., R. Giorgi, and P. Baglioni. 2006. "Nanotechnology for Vasa Wood De-acidification." *Macromolecular Symposia* 238 (1): 30–36. <https://doi.org/10.1002/masy.200650605>.
- Cremonesi, P. 2023. "A Note of Caution on the Use of Calcium Nanoparticle Dispersions as Deacidifying Agents." *Studies in Conservation* 68 (2): 128–135. <https://doi.org/10.1080/00393630.2021.2002023>.
- Forney, C. F., and D. G. Brandl. 1992. "Control of Humidity in Small Controlled-Environment Chambers Using Glycerol-Water Solutions." *Horttechnology* 2 (1): 52–54. <https://doi.org/10.21273/HORTTECH.2.1.52>.
- Giorgi, R., C. Bozzi, L. Dei, C. Gabbiani, B. W. Ninham, and P. Baglioni. 2005. "Nanoparticles of Mg(OH)₂: Synthesis and Application to Paper Conservation." *Langmuir* 21 (18): 8495–8501. <https://doi.org/10.1021/la050564m>.
- Giorgi, R., D. Chelazzi, and P. Baglioni. 2005. "Nanoparticles of Calcium Hydroxide for Wood Conservation. The Deacidification of the Vasa Warship." *Langmuir* 21 (23): 10743–10748. <https://doi.org/10.1021/la0506731>.
- Giorgi, R., D. Chelazzi, E. Fratini, S. Langer, A. Niklasson, M. Rådemar, J.-E. Svensson, and P. Baglioni. 2009. "Nanoparticles of Calcium Hydroxide for Wood Deacidification: Decreasing the Emissions of Organic Acid Vapors in Church Organ Environments." *Journal of Cultural Heritage* 10 (2): 206–213. <https://doi.org/10.1016/j.culher.2008.06.012>.
- Giorgi, R., L. Dei, M. Ceccato, C. Schettino, and P. Baglioni. 2002. "Nanotechnologies for Conservation of Cultural Heritage: Paper and Canvas Deacidification." *Langmuir* 18 (21): 8198–8203. <https://doi.org/10.1021/la025964d>.
- Giorgi, R., L. Dei, C. Schettino, and P. Baglioni. 2002. "A New Method for Paper Deacidification Based on Calcium Hydroxide Dispersed in Nonaqueous Media." In *Works of Art on Paper, Books, Documents and Photographs: Techniques and Conservation*, edited by V. Daniels, A. Donnithorne, and P. Smith, 69–73. Baltimore: International Institute for Conservation. <https://doi.org/10.1179/sic.2002.47.s3.014>.
- Horst, T. H., R. D. Smith, A. Potthast, and M. A. Hubbe. 2020. "Accelerated Aging of Deacidified and Untreated Book Paper in 1967 Compared with 52 Years of Natural Aging." *Restaurator. International Journal for the*

- Preservation of Library and Archival Material* 41 (3): 131–152. <https://doi.org/10.1515/res-2020-0006>.
- Khawam, A., and D. R. Flanagan. 2006. "Solid-State Kinetic Models: Basics and Mathematical Fundamentals." *The Journal of Physical Chemistry B* 110 (35): 17315–17328. <https://doi.org/10.1021/jp062746a>.
- Lunjakorn, A., M. Mattea-Coco, P. Thirvengadam, H. Silvo, K. Adriana, K. Rupert, S.-K. Karin, and M. Tamilselvan. 2018. "Nano-Structures & Nano-Objects Strengthening of Paper by Treatment with a Suspension of Alkaline Nanoparticles Stabilized by Trimethylsilyl Cellulose." *Nano-Structures & Nano-Objects* 16: 363–370. <https://doi.org/10.1016/j.nanoso.2018.09.009>.
- Madejová, J. 2003. "FTIR Techniques in Clay Mineral Studies." *Vibrational Spectroscopy* 31 (1): 1–10. [https://doi.org/10.1016/S0924-2031\(02\)00065-6](https://doi.org/10.1016/S0924-2031(02)00065-6).
- Nanorestore Paper Technical Data Sheet. 2016 https://www.csgi.unifi.it/products/downloads/paper_ts_eng.pdf.
- Nourinaeini, S., G. Poggi, A. Parmentier, G. Rogati, P. Baglioni, and F. De Luca. 2020. "Reconditioning Acidic and Artificially Aged Cellulose with Alkaline Nanoparticles: An NMR Diffusometry Study." *Cellulose* 27 (13): 7361–7370. <https://doi.org/10.1007/s10570-020-03298-0>.
- Palladino, N., M. Hacke, G. Poggi, O. Nechyporchuk, K. Kolman, Q. Xu, M. Persson, et al. 2020. "Nanomaterials for Combined Stabilisation and Deacidification of Cellulosic Materials—The Case of Iron-Tannate Dyed Cotton." *Nanomaterials* 10 (5): 900. <https://doi.org/10.3390/nano10050900>.
- Poggi, G., P. Baglioni, and R. Giorgi. 2011. "Alkaline Earth Hydroxide Nanoparticles for the Inhibition of Metal Gall Ink Corrosion." *Restaurator* 32 (3): 247–273. <https://doi.org/10.1515/rest.2011.012>.
- Poggi, G., R. Giorgi, A. Mirabile, H. Xing, and P. Baglioni. 2017. "A Stabilizer-Free Non-Polar Dispersion for the Deacidification of Contemporary Art on Paper." *Journal of Cultural Heritage* 26: 44–52. <https://doi.org/10.1016/j.culher.2017.02.006>.
- Poggi, G., R. Giorgi, N. Toccafondi, V. Katzur, and P. Baglioni. 2010. "Hydroxide Nanoparticles for Deacidification and Concomitant Inhibition of Iron-Gall Ink Corrosion of Paper." *Langmuir* 26 (24): 19084–19090. <https://doi.org/10.1021/la1030944>.
- Poggi, G., A. Parmentier, S. Nourinaeini, and F. De Luca. 2020. "Detection of Acidic Paper Recovery After Alkaline Nanoparticle Treatment by 2D NMR Relaxometry." *Magnetic Resonance in Chemistry* 58 (9): 902–912. <https://doi.org/10.1002/mrc.5063>.
- Poggi, G., M. C. Sistach, E. Marin, J. F. Garcia, R. Giorgi, and P. Baglioni. 2016. "Calcium Hydroxide Nanoparticles in Hydroalcoholic Gelatin Solutions (GeolNan) for the Deacidification and Strengthening of Papers Containing Iron Gall Ink." *Journal of Cultural Heritage* 18: 250–257. <https://doi.org/10.1016/j.culher.2015.10.005>.
- Poggi, G., N. Toccafondi, D. Chelazzi, P. Canton, R. Giorgi, and P. Baglioni. 2016. "Calcium Hydroxide Nanoparticles from Solvothermal Reaction for the Deacidification of Degraded Waterlogged Wood." *Journal of Colloid and Interface Science* 473: 1–8. <https://doi.org/10.1016/j.jcis.2016.03.038>.
- Poggi, G., N. Toccafondi, L. N. Melita, J. C. Knowles, L. Bozec, R. Giorgi, P. Baglioni, and P. Baglioni. 2014. "Calcium Hydroxide Nanoparticles for the Conservation of Cultural Heritage: New Formulations for the Deacidification of Cellulose-Based Artifacts." *Applied Physics A* 114 (3): 685–693. <https://doi.org/10.1007/s00339-013-8172-7>.
- Rodriguez-Navarro, C., K. Elert, and R. Ševčík. 2016. "Amorphous and Crystalline Calcium Carbonate Phases During Carbonation of Nanolimes: Implications in Heritage Conservation." *CrystEngComm* 18 (35): 6594–6607. <https://doi.org/10.1039/C6CE01202G>.
- Sharma, G., W. Wu, and E. N. Dalal. 2005. "The CIEDE2000 Color-Difference Formula: Implementation Notes, Supplementary Test Data, and Mathematical Observations." *Color Research & Application* 30 (1): 21–30. <https://doi.org/10.1002/col.20070>.
- Smith, B. C. 2018. "The C=O Bond, Part VIII: Review." *Spectroscopy* 33 (11): 24–29.
- Thomas, J. J. 2007. "A New Approach to Modeling the Nucleation and Growth Kinetics of Tricalcium Silicate Hydration." *Journal of the American Ceramic Society* 90 (10): 3282–3288. <https://doi.org/10.1111/j.1551-2916.2007.01858.x>.
- Tironi, A., M. A. Trezza, E. F. Irassar, and A. N. Scian. 2012. "Thermal Treatment of Kaolin: Effect on the Pozzolanic Activity." *Procedia Materials Science* 1: 343–350. <https://doi.org/10.1016/j.mspro.2012.06.046>.
- Witzel, R. F., R. W. Burnham, and J. W. Onley. 1973. "Threshold and Suprathreshold Perceptual Color Differences." *Journal of the Optical Society of America* 63 (5): 615. <https://doi.org/10.1364/JOSA.63.000615>.
- Xu, Q., G. Poggi, C. Resta, M. Baglioni, and P. Baglioni. 2020. "Grafted Nanocellulose and Alkaline Nanoparticles for the Strengthening and Deacidification of Cellulosic Artworks." *Journal of Colloid and Interface Science* 576: 147–157. <https://doi.org/10.1016/j.jcis.2020.05.018>.
- Young, J. F. 1967. "Humidity Control in the Laboratory Using Salt Solutions—a Review." *Journal of Applied Chemistry* 17 (9): 241–245. <https://doi.org/10.1002/jctb.5010170901>.
- Zervos, S., and I. Alexopoulou. 2015. "Paper Conservation Methods: A Literature Review." *Cellulose* 22 (5): 2859–2897. <https://doi.org/10.1007/s10570-015-0699-7>.
- Zhbankov, R. G. 1995. *Infrared Spectra of Cellulose and its Derivatives*. Boston, MA: Springer US. <https://doi.org/10.1007/978-1-4899-2732-3>.
- Zumbühl, S., and S. Wuelfert. 2001. "Chemical Aspects of the Bookkeeper Deacidification of Cellulosic Materials: The Influence of Surfactants." *Studies in Conservation* 46 (3): 169–180. <https://doi.org/10.2307/1506808>.