

The application of scanning microscopy in studies on paper deacidification using magnesium hydroxide nanoparticles

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Abstract: *The application of scanning microscopy in studies on paper deacidification using magnesium hydroxide nanoparticles.* The aim of this study was to find differences of magnesium hydroxide nanopowder deposition in deacidified paper. A scanning electron microscope with SE and BSE detectors was applied. The results showed that magnesium hydroxide deposition depends on the size of its particles and concentration of the dispersion. The particles observed on the paper surface differ in size from nano- to submicro- and microstructures.

Keywords: scanning microscopy, paper conservation, deacidification, magnesium hydroxide, nanoparticles

INTRODUCTION

Archival documents, library collections and works of art made from the so-called acid paper, accumulated for over 150 years, are at risk of destruction as a result of cellulose hydrolysis processes, with accompanying oxidation reactions constituting an additional degradation factor (Baty et al. 2010). Deacidification of paper and the formation of alkaline reserves may be a method capable of retarding degradation processes. Many techniques of mass deacidification apply magnesium compounds as the alkaline agent. Paper conservators focused on simple magnesium compounds, such as MgO and Mg(OH)₂, many years ago. These compounds are known for their capacity to stabilise free radicals, hydroxides may form alkaline reserves, but their disadvantage is poor water solubility, hindering penetration into the porous structure of paper. Efficiency of penetration of these compounds into paper structure may be improved by their introduction as nanoparticles in dispersifying solutions, such as e.g. alcohols (Stefanis and Panayiotou 2007, 2008, 2010). The aim of this study was to compare the effects of paper deacidification with standard Mg(OH)₂ and its nanoparticles using scanning microscopy.

MATERIAL

The deacidifier applied in this experiment was composed of Mg(OH)₂ nanoparticles (p.f.a., 99.8 % trace metal basis, Aldrich, No. 632309), with particle size of <100 nm (laser PSA, TEM, XRD analyses). For comparative purposes paper samples were also deacidified using standard Mg(OH)₂ (p.f.a. 99%, Fluka, No. 63087).

Analyses were conducted on model paper, i.e. Whatman 3Chr MM filter paper. Initial pH (cold water) of filter paper was 7.36. Samples of 4 × 4 cm were cut from the filter paper. These samples were acidified with H₂SO₄ solution to pH 4.8 (determined in cold water extract). After samples had been dried between filter paper sheets, they were left at room temperature for 10 days. Acidified samples, after their moisture content had been determined, were deacidified with a dispersion of Mg(OH)₂ nanoparticles in 2-propanol. Analyses were conducted using dispersions at a concentration of 0.0125% or 0.1% Mg(OH)₂, which were introduced in the form of bath (2×0.5 h) and deacidified to pH 7.93. Following deacidification filter paper samples were again placed between filter paper sheets and slightly

pressed with a sheet of neutral cardboard in order to ensure surface smoothness. Analyses were conducted on paper samples at 10 days after the completion of deacidification (to facilitate the formation of alkaline reserves as a result of absorption of CO₂ from air with magnesium carbonate).

METHODS

Effectiveness of acidification and deacidification of paper samples was controlled by analysing pH of aqueous extract (Tappi T 509 om-02).

Paper samples were examined under a scanning electron microscope (SEM) LEO Electron Microscopy 1430 VP. Samples were analysed under the microscope both non-sputtered and Au sputtered, with a SE (Secondary Electron) detector used in the latter case. Magnesium distribution on sample surface was assessed using a scanning microscope coupled with a Backscattered Electron (BSE) detector.

RESULTS AND DISCUSSION

Preliminary analyses were conducted using SEM-SE on powder samples of the standard reagent and Mg(OH)₂ nanoparticles. Images showed a marked difference in the shape and dimensions of particles. Nanoparticles formed irregular crystallites (Figure 1a) or agglomerates of sizes smaller than that of the standard reagent, forming round or rhomboidal particles (Figures 1b). Both reagents were characterised by varied sizes of particles. Next to larger agglomerates smaller particles of submicron dimensions could be observed (Figures 1a and 1b). Nanoparticles are known for their capacity to form agglomerates; however, from the point of view of paper deacidification it is essential for nanoparticle agglomerates to fall within the range of submicron dimensions, i.e. below 800 nm. Due to the size of pores in paper (between 400 and 800 nm) this particle size is sufficient for them to penetrate into paper structure. It needs to be stressed that nanoparticles are introduced to paper as dispersions in 2-propanol, ground and homogenised by mechanical mixing or the ultrasound technique. Such a method of their introduction to paper aims at the reduction of agglomerate size and possible increase in hydroxide comminution.

Successive images indicate the potential for observation of magnesium particles under a microscope with a BSE attachment. This method makes it possible to distinguish elements on sample surface in terms of the differences in their atomic number (for number over 12). These differences represent different shades of grey, with lightness increasing with the atomic number. SEM-BSE microscopy made it possible to observe differences in deacidification efficiency depending on the type of applied reagent (standard vs. nanopowder) - in Figures 2a and 2b we may clearly see that magnesium hydroxide particles accumulating on the surface are larger in the case of the standard reagent (Figure 2a) than in the case of nanopowder (Figure 2b). Marked variability in the amount of the introduced deacidifier depending on the concentration of deacidifying dispersion is shown in Figures 3a and 3b, taken under a SEM microscope with an SE detector. This technique makes it possible to obtain images with greater resolution. It may be seen in Figures 3a and 3b that when applying greater dispersion concentrations the effect of partial “glueing” of sample surface may be obtained. Presented photographs show to a certain extent the process of precipitation of these above mentioned larger particles of magnesium hydroxide on paper surface. Although a considerable amount of the hydroxide dispersion is precipitated in the form of agglomerates on sample surface, it needs to be observed that these particles may react with sulphuric acid present in paper and undergo transformation to magnesium carbonate under the influence of CO₂ from air (after approx. 10 days from deacidification). In order to assess penetrability into paper pores for particles with nanometric dimensions, analyses were also conducted at larger magnifications applying gold sputtering of samples. In Figures 4a and 4b we may see particles with

submicron (Figure 4a) and nanometric dimensions (Figure 4b). Although microscopic analysis is burdened with the error of partiality, conducted analyses suggest that also particles with dimensions close to nanometric may penetrate into paper structure, thus enhancing effectiveness of deacidification of slightly soluble magnesium hydroxide.

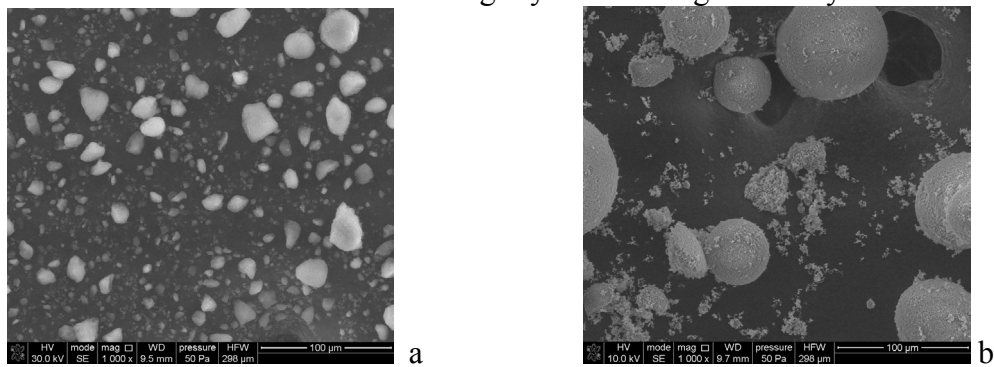


Fig.1. SEM-SE images of nanoparticles-agglomerates (a) and conventional $Mg(OH)_2$ particles (b).

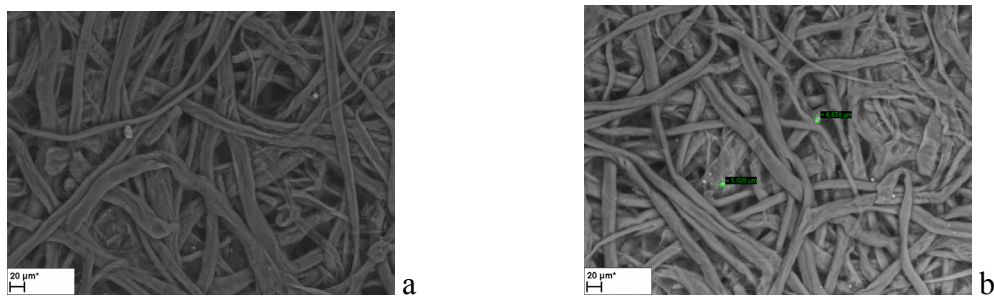


Fig.2 SEM-BSE images of conventional magnesium hydroxide (a) and nanoparticles of $Mg(OH)_2$ deacidifier (b).

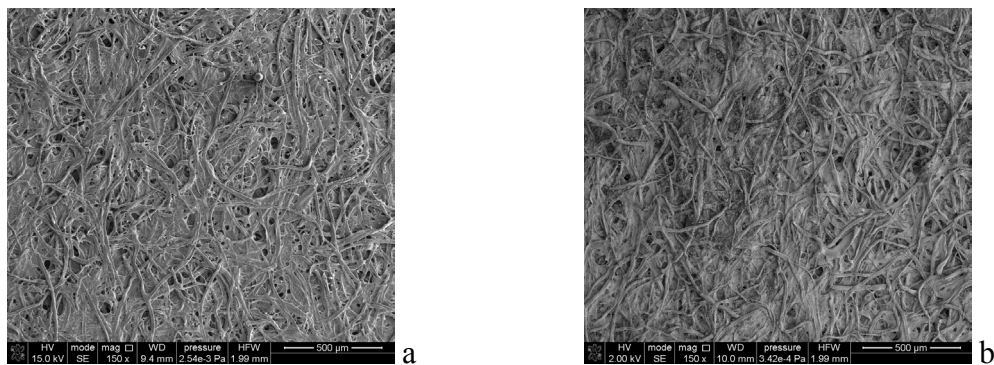


Fig. 3. Paper after deacidification with 0.0125% (a) and 0.1% (b) dispersion of $Mg(OH)_2$ nanopowder (SEM-SE images).

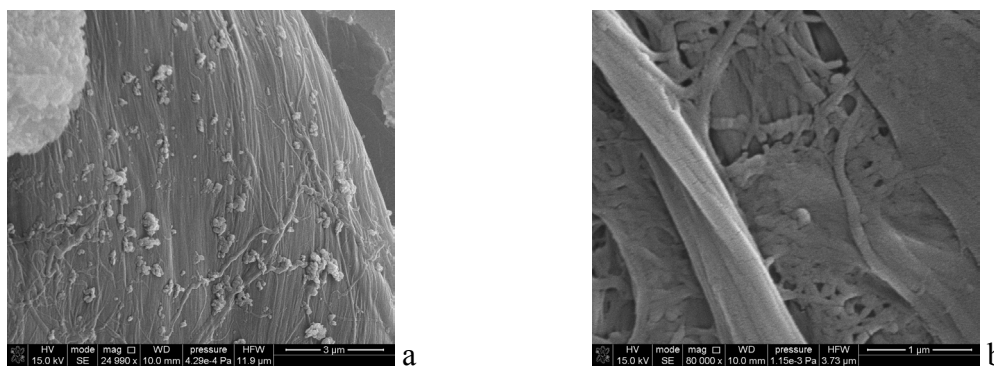


Fig. 4. Micro-, submicro-(a) and nanoparticles of magnesium hydroxide (b) on the paper sample surface (SEM-SE images).

CONCLUSION

Analysis using a scanning microscope with SE and BSE attachments proved to be suitable for assessment of paper deacidification with $\text{Mg}(\text{OH})_2$ nanopowder. The SEM-BSE technique makes it possible to distinguish particles of magnesium compounds on paper surface. The SEM-SE technique made it possible to show the effect of the amount and type of reagent (standard vs. nanopowder) on paper deacidification.

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Streszczenie: *Zastosowanie mikroskopii skaningowej w badaniach nad odkwaszaniem papieru nanocząsteczkami wodorotlenku magnezu.* Celem pracy było porównanie efektywności odkwaszania papieru wodorotlenkiem magnezu o mikrometrycznych i nanometrycznych rozmiarach cząsteczek. Stosowano mikroskop skaningowy z przystawkami SE i BSE. Analizy wykazały poziom zróżnicowania rozmiarów cząsteczek związków magnezu oraz ich ilości na powierzchni w zależności od rodzaju odczynnika odkwaszającego i jego stężenia.

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