

DEACIDIFICATION OF PAPER WITH $Mg(OH)_2$ NANOPARTICLES: THE IMPACT OF DOSAGE ON PROCESS EFFECTIVENESS

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ABSTRACT

The aim of the work was to analyse the influence of $Mg(OH)_2$ nanoparticle dosage on the deacidification process, especially in relation to paper permanence. Samples of model papers were characterised by SEM-EDX and XPS methods which proved effective neutralisation. The influence of the suspension concentration was evaluated on cellulose DP and on the optical properties after the paper thermal ageing process. Generally, the protective effect of deacidification increased along with an increased dosage of the magnesium hydroxide nanoparticles in artificially acidified paper samples and in papers covered with iron gall ink.

INTRODUCTION

Paper deacidification remains one of the most important issues in the challenge of preserving the cultural heritage of mankind. Various deacidification procedures have been elaborated in order to protect this paper-based heritage (Baty et al. 2010). With regard to the solvents that are used, deacidification may be divided into aqueous and non-aqueous treatment. For the non-aqueous system, when liquid suspensions are used, efficiency of the treatment depends on the deacidifier's efficient penetration into the fibre structure. That is why nanoparticles have attracted the interest of conservators as a potential application instead of conventional, micro-sized hydroxide particles (Anders and Becker 2000, Baglioni et al. 2013, Giorgi et al. 2002, 2005, Poggi et al. 2010, 2011, Sequeira et al. 2006). Among the experimental data that have been published so far, studies on the application of $Mg(OH)_2$ nanoparticles have attracted less attention (Giorgi et al. 2002, 2005) and are frequently treated as auxiliary for experiments with calcium hydroxide (Stefanis and Panayiotou, 2007, 2008, 2010). Magnesium compounds are potentially interesting for conservation purposes because they show stabilising properties in relation to cellulose subjected to oxidising treatment (Lapierre et al. 2000, Wójciak et al. 2007), and acid degradation of paper is always accompanied by oxidation processes. Most published studies have showed the effectiveness

of deacidification by hydroxide nanoparticles based only on paper pH measurements which are rather intermediate and do not always constitute precise methods of analysis (Strlič et al. 2004). In this work we used spectroscopic techniques such as XPS and SEM-EDX which allow for a more direct evaluation of the neutralisation effects.

Authors describing the effectiveness of paper deacidification with the use of $\text{Mg}(\text{OH})_2$ nanoparticles have monitored the strength and optical properties or DP (Giorgi et al. 2002, 2005, Stefanis and Panayiotou, 2007, 2008, 2010), however, none of the published studies have related such data to the amount of introduced deacidifier. This is an important question because the amount of alkali determines the final pH of the paper. There is a shortage of comparative sources of information showing how the level of pH after deacidification influences paper permanence. The alkalinity of paper is crucial for its stability after deacidification and is particularly important in the case of papers covered with metal-gall inks (Poggi et al. 2010). The excess of alkali may be detrimental because of the high catalytic activities of transition-metal ions at ca. 8 pH for iron and pH > 8.5 for copper (Strlič et al. 2003).

The aim of this work is to present the results of comparative studies indicating the influence of $\text{Mg}(\text{OH})_2$ nanoparticle dosage on the effectiveness of model paper deacidification, including paper samples covered with iron gall ink.

MATERIAL AND METHODS

Material

Deacidifier

Nanoparticles of $\text{Mg}(\text{OH})_2$ (Aldrich, No 632309) with dimensions below 100 nm (as measured by laser Particle Size Analysis, TEM, XRD) were used as the deacidifier. The TEM image shows the size of the flat-shaped $\text{Mg}(\text{OH})_2$ particles (Fig. 1). Qualitative and quantitative analysis using TEM with an EDX spectrometer confirmed that magnesium and oxygen are the essential components of the particles used.

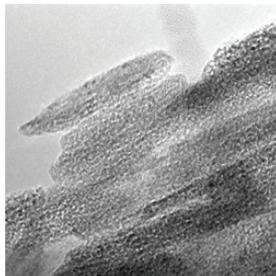


Fig. 1: TEM image of $\text{Mg}(\text{OH})_2$ nanoparticles used for paper deacidification.

Model paper

In the case of some historic acidic papers, even small amounts of magnesium compounds can hinder the evaluation of deacidification with $\text{Mg}(\text{OH})_2$, especially when sensitive spectroscopic methods are used. That is why in this work we chose as the model paper chemically pure, artificially acidified Whatman 3Chr MM filter paper 0.35 mm in thickness and with a grammage of 180, composed of 98 % α -cellulose made from cotton fibres. The initial pH (cold water extract) of the Whatman paper was 7.36, and in it only traces of magnesium (<5 ppm) were

determined by the AAS method. After acidification, even trace amounts of magnesium could not be detected, i.e. the level in mass % amounting to 0.03 % (SEM-EDX) means that, practically, there was no magnesium on the surface of the acidified paper. Spectra produced by the automatic method and with a “forced” magnesium peak provided similar results. The XPS spectra also did not show the presence of Mg on the surface of the acidified samples.

Acidification and deacidification

The paper was cut into samples of 4x4 cm. The samples were acidified for 34 h with aqueous H₂SO₄ solution (pH 2.07) at room temperature. The ratio of paper sample to H₂SO₄ solution was 1:50 (w/v). Then the samples were dried between sheets of blotting paper and were left at room temperature for 10 days to dry out. After determining the moisture content, acidified paper samples were treated with 100 cm³ dispersion of Mg(OH)₂ nanoparticles in 2-propanol. Shortly before deacidification, the dispersion was homogenised for 5 min using a magnetic stirrer. Dispersion was applied using the following washing methods: 8 samples were placed on Petri dishes, immersed in dispersion and deacidified for 0.5 h, then they were turned over and deacidified again for 0.5 h. Different variants of dispersion concentrations were used: 0.0125, 0.025, 0.05, 0.1, 0.3, 0.6, 0.9 and 1.2 %. After deacidification the paper samples were placed again between neutral Whatman paper sheets and pressed slightly with a sheet of neutral cardboard (pressure of 1.2 g.cm⁻²) in order to provide a smooth surface.

Analyses were performed on paper samples 10 days after the completion of deacidification in order to facilitate the formation of an alkaline reserve as a result of CO₂ absorption from the air.

Some of the paper samples were not acidified by H₂SO₄ but immersed (3 sec) in iron gall ink. These samples were dried and deacidified as above. A part of the samples covered with iron gall ink was deacidified multiple times (immersed 4 times for 3 sec in the following dispersion concentrations: 0.0125, 0.025, 0.05 and 0.1 %) in order to obtain, in a controlled manner, a range of paper pH from 4 to 8.5. Iron gall ink was prepared by following the Neevel method (Neevel 1995).

Accelerated ageing procedures

Thermal ageing

After deacidification, parts of the paper samples, together with PET/Al/PE composite foil bags, were conditioned for one week at 20 ± 1°C and at a relative humidity (RH) of 65 %. After conditioning, the same masses of paper samples were encapsulated inside the PET/Al/PE bags by sealing them with the use of an FKR-200.300 impulse sealer (Jablonský et al. 2011). Double sealing of all edges was performed in order to assure the system's air-tightness during the accelerated ageing tests. The bags were then put into an ageing chamber (WAMED) and kept for 5 h (papers acidified with H₂SO₄ had a starting pH of 4.45) or for 15 min (samples covered with iron gall ink with a starting pH of 2.05 and 3.50) at a temperature of 80±0.1°C and a humidity of ca. 65 %. The times of ageing were shortened for samples covered with iron gall ink since after 5 h of thermal treatment the samples showed the onset of carbonisation. After ageing the papers were conditioned for testing once again.

Methods

pH measurements

Both acidification and deacidification were controlled by pH analyses of cold water extracts (TAPPI T 509 om-02). An Elmetron CP 401 pH-meter accurate to ±0.01 was applied. The reactions of paper samples covered with iron gall ink and then deacidified to a controlled pH by

multiple immersions were additionally measured by the surface method using a Mettler Toledo SevenEasy pH-meter.

SEM-SE-BSE-EDX

The paper samples were observed by scanning electron microscopy (SEM) under a LEO Electron Microscope 1430 VP. The samples were analysed under a microscope, both un-sputtered and sputtered, with a thin gold (Au) layer deposited under a vacuum – a Secondary Electron (SE) detector was used in the latter case. The distribution of magnesium on the sample surface was assessed using a scanning microscope with a Backscattered Electron (BSE) detector, while quantitative analyses of magnesium on the surface of the paper were conducted using an Energy Dispersive X-ray (EDX) spectrometer (Quantax 200) coupled with an XFlash 410 detector (BrukerAXS). A magnesium content above 0.5 [mass %] was accepted for quantitative evaluation of the SEM-EDX results.

AAS

Total magnesium content in the tested papers was determined by atomic absorption spectrometry (AAS SavantAA Σ , GBC Scientific Equipment). The papers were mineralised in a microwave mineraliser (Milestone ETHOS 1) in a mixture of 7 ml 65 % HNO₃ and 1 ml 30 % H₂O₂.

XPS

Measurements were performed with a VG Scientific photoelectron spectrometer ESCALAB-210 using Al K α radiation (1486.6 eV) from an X-ray source operating at 15 kV and 20 mA. Survey spectra were recorded for all samples in an energy range from 0 to 1350 eV with 0.4 eV step. High resolution spectra were recorded with 0.1 eV step, 100 ms dwell time and 25 eV pass energy. A ninety-degree take-off angle was used in all measurements. Aromatic carbon C 1s peak at 284.5 eV was used as a reference of the binding energy. Curve fitting was performed using AVANTAGE software provided by Thermo Electron, which describes each component of the complex envelope as a Gaussian–Lorentzian sum function; a constant 0.3(\pm 0.05) G/L ratio was used. The background was fitted using the non-linear Shirley model. Scofield sensitivity factors and measured transmission function were used for quantification.

Degree of polymerisation (DP)

The degree of polymerisation (DP) of cellulose from the model papers was measured using the viscosimetric method (TAPPI T 230 om-89). Standard deviation (σ) for three independent measurements was less than $\pm 5.3 \text{ cm}^3 \cdot \text{g}^{-1}$.

Optical properties

The optical properties (brightness) of the paper were tested with the use of an L&W ELREPHO 2000 spectrometer following the ISO 2470 standard method and colour measurements following CIE L*a*b* colour space. The same paper samples were measured before deacidification, after deacidification and after thermal ageing; the same place of the paper surface was analysed. Three different paper samples were measured 5 times for every kind of treatment or for references (together 15 observations were made for every kind of treatment or for references). Kruskal-Wallis and Mann-Whitney non-parametric tests or a multiple comparison test were used to determine any significant differences between the mean results (significant for $p < 0.05$).

RESULTS AND DISCUSSION

Effect of neutralisation - SEM-EDX and XPS studies

An earlier SEM-BSE analysis had shown that after deacidification magnesium compounds were found in quite a large number on the paper surface in the form of agglomerates with micrometric particle dimensions, and only when using bigger magnification also as nano-sized particles (Wójciak 2015). The above-mentioned information justified posing the question as to what the chemical nature of those deposits was and what the extent of the neutralising action of the $\text{Mg}(\text{OH})_2$ nanoparticles was? Nanoparticles are solids used in dispersed phase, that is why we decided to examine whether the magnesium compounds observed on the paper surface may also have been (if not only) the products of neutralisation reactions between the magnesium hydroxide nanoparticles and the sulfuric acid molecules present in the papers.

Using SEM-EDX microscopy, it was shown that some particles, deposited on the paper after deacidification, were composed of magnesium and sulfur (Fig. 2). Quantitative SEM-EDX measurements suggest that the rich sulfur deposits were the result of possible interaction between the magnesium hydroxide nanoparticles and the sulfur-containing compounds; for example, 10.52 At. % (Atomic percentage) of magnesium and 3.67 At. % of sulfur on the particle surface deposited on acidified paper versus 25.31 At. % of magnesium exclusively on the particle observed for the non-acidified paper sample. The particles studied by using the SEM-EDX method were relatively large and represented the part of the dispersion which could form agglomerates and/or transform as a result of a neutralisation reaction.

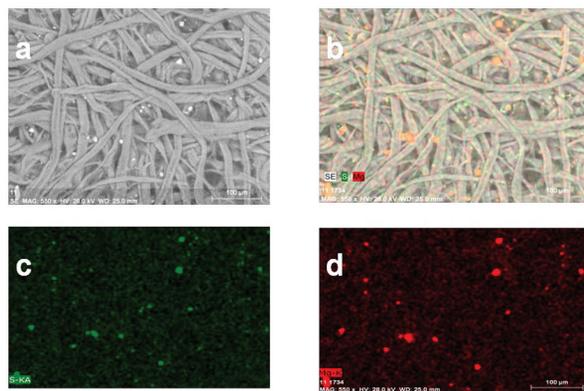


Fig. 2: Comparison of Mg and S detection on paper sample deacidified with dispersion containing 0.0125 % $\text{Mg}(\text{OH})_2$ nanoparticles in 2-propanol: a) SEM-BSE image - magnesium compounds particles distinguished based on the light shade of gray, b) SEM-EDX image with common Mg and S detection, c) SEM-EDX image with S detection only, d) SEM-EDX image with Mg detection only.

More definite data were obtained using the XPS method. Typical XPS survey results for the deacidified paper are shown in Fig. 3a. In addition to cellulosic peaks due to C and O, peaks due to Mg are also observed. All the other spectra looked quite similar; the list of samples is given in Tab. 1.

Tab. 1: Quantitative (XPS) and qualitative (XPS/AAS) analysis of paper samples deacidified with various $Mg(OH)_2$ charges (pH of paper before deacidification - 4.45).

Concentration of $Mg(OH)_2$ in dispersion (%)	Methods				
	pH after deacidification	AAS	XPS		
		Mg content in papers (ppm)	Mg2p peak BE (eV)	At. (%)	Suggested state
0.1	8.87	72.4 ± 3.5	50.43	1.28	Mg^{+2} (MgO)
0.6	10.10	312.6 ± 2.7	50.82	2.44	Mg^{+2} ($MgSO_4$)
1.2	10.80	462.1 ± 2.1	50.78	3.91	Mg^{+2} ($MgSO_4$)

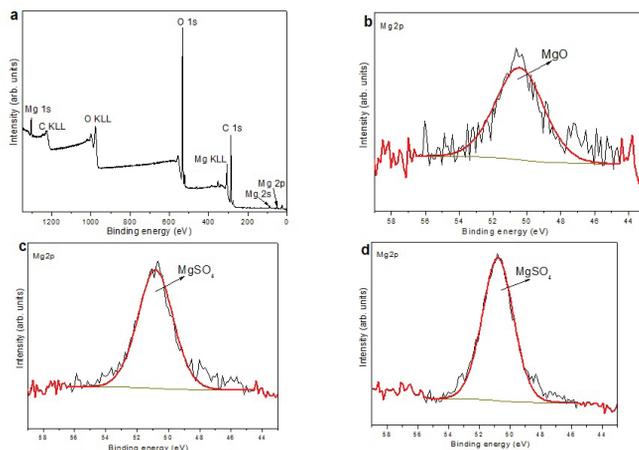


Fig. 3: XPS spectra of paper deacidified with various concentration of $Mg(OH)_2$ in dispersion: a) the whole survey spectra - 0.6 % $Mg(OH)_2$ used, b) $Mg2p$ spectrum - 0.3 % of $Mg(OH)_2$ used, c) $Mg2p$ spectrum - 0.6 % of $Mg(OH)_2$ used, d) $Mg2p$ spectrum - 1.4 % of $Mg(OH)_2$ used.

High-resolution spectra for the $Mg2p$ regions of three different samples are shown in Figs. 3b-d. The binding energy of the peak at 50.43 (Fig. 3b) corresponds to $MgO/Mg(OH)_2$, while those at 50.82 (Fig. 3c) and 50.78 (Fig. 3d) are attributed to $MgSO_4$ (Moulder et al. 1992, Wang and Xiong 2012). At least in the case of samples treated with dispersions containing above 0.6 % of $Mg(OH)_2$ (Figs. 3c and 3d, respectively), these results confirm the neutralisation of hydroxide as a consequence of a reaction with the sulfur-containing compounds. Taking into consideration the relatively high content of sulfuric acid in artificially acidified papers, it is most likely that the magnesium sulfate was formed via a reaction between magnesium hydroxide and sulfuric acid and not, or to a lesser extent, with SO_2 from air, which is a process that is also possible (Wang and Xiong 2012). Another problem, i.e. the extent of the neutralisation reactions, needs further study. Alkaline nanoparticles are solids and may react with the acidic molecules that are present in their close environment. We can assume that nanoparticles may not be able to neutralise all of the acid molecules present in the paper, especially inside the fibres. Such an assumption raises the question whether by increasing the concentration of the dispersion better results of deacidification can be achieved. Another question is how the alkali dosage will affect the permanence of the paper.

The XPS studies of the paper samples treated with various concentrations of $Mg(OH)_2$ showed, generally, that the content of magnesium on the paper surface increased when a higher

amount of deacidifier was used. The exception was the sample that had been deacidified with the lowest concentration of dispersion used in the studies (0.3 %), in which the presence of chemical bond characteristics only for $\text{Mg}(\text{OH})_2$ and/or MgO were confirmed. Such data were obtained despite the fact that measurements of pH after deacidification showed the effectiveness of this treatment (Tab. 2).

Tab. 2: pH and DP_{visc} of paper samples after deacidification with $\text{Mg}(\text{OH})_2$ and thermal ageing (pH of samples after artificial acidification - 4.45).

Measurements	Concentration of $\text{Mg}(\text{OH})_2$ in dispersion (%)				
	Reference (not acidified)	0.0125	0.025	0.05	0.1
Paper samples not covered with iron gall ink					
pH after deacidification and ageing (cold water extract)	7.01	8.46	9.08	10.22	10.54
DP_{visc}	794	526	622	693	730
Paper samples covered with iron gall ink					
pH after 1 x deacidification (cold water extract)	2.05	3.41	3.68	3.76	4.12
DP_{visc}	261	310	359	367	373
pH after 4 x deacidification (contact method)	3.50	4.28	5.40	6.77	8.71
DP_{visc}	533	546	571	599	664

It should be noticed that although some amounts of nanoparticles were not neutralised, by forming an alkaline reserve they were still able to absorb SO_2 , which can prevent degradation of paper by acidic oxides from the air. Better results of the qualitative analysis, confirming the neutralisation reactions, were obtained using a higher concentration of $\text{Mg}(\text{OH})_2$. Although these data favour deacidification with higher dosages of $\text{Mg}(\text{OH})_2$, the superficial character of the XPS determinations and the fact that only a relatively small part of the sample may be analysed (in relation to the total surface of the paper sample) prevent us from making conclusions whether the papers were successfully deacidified or not.

Magnesium compound distribution - microscopic studies

Spectroscopic analysis showed a correlation between pH and the magnesium content in the deacidified paper samples (Tab. 1). The pH increased together with a growing magnesium content which was determined on the surface (XPS) and in the whole paper volume (AAS). These results proved that if not all then at least a part of the acids present in the paper were neutralised, and that the part of magnesium hydroxide that is sparingly soluble in water was transferred into the extracts and yielded an alkaline reaction. Magnesium hydroxide as a polar compound introduced with a slightly polar solvent (2-propanol) does not form a true solution but may form dispersion as a result of solvation. A polar solvent facilitates the swelling of fibres; therefore the $\text{Mg}(\text{OH})_2$ nanoparticles should interact more easily with the porous structure of the paper and the paper's fibres. We used the SEM-BSE and SEM-SE techniques in order to better understand the question regarding magnesium distribution in paper after deacidification. As can be observed in Figs. 4-7, along with an increasing dosage of the deacidifier the surface of the paper samples was increasingly more covered.

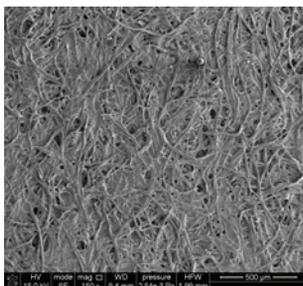


Fig. 4: SEM-SE image of deposits on paper surface after deacidifying washing with 0.3 % $Mg(OH)_2$ dispersion in 2-propanol.

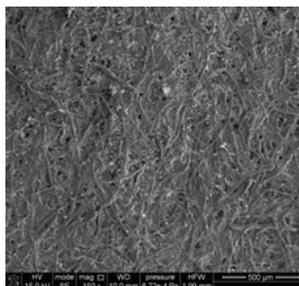


Fig. 5: SEM-SE image of deposits on paper surface after deacidifying washing with 1.4 % $Mg(OH)_2$ dispersion in 2-propanol.

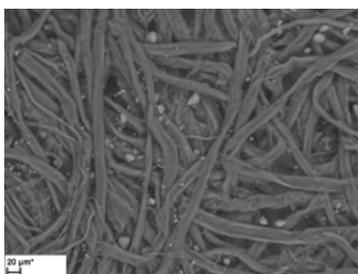


Fig. 6: SEM-BSE image of deposits on paper surface after deacidifying washing with 0.6 % $Mg(OH)_2$ dispersion in 2-propanol.

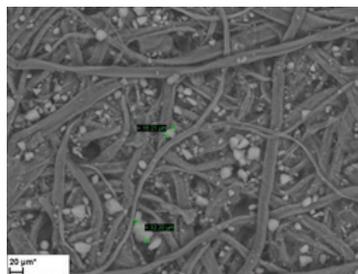


Fig. 7: SEM-BSE image of deposits on paper surface after deacidifying washing with 1.4 % $Mg(OH)_2$ dispersion in 2-propanol.

However, photos taken at larger magnification and with the SE detector (Fig. 8) showed that although the magnesium compounds created deposits, they mostly did not form a “film” on the paper surface. Structures observed at larger magnification are agglomerates of various sizes, from micro to nanometric dimensions.

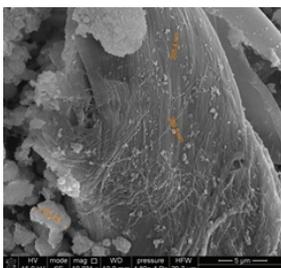


Fig. 8: SEM-SE image of deposits on paper surface after deacidifying washing with 1.4 % $Mg(OH)_2$ dispersion in 2-propanol (magnification 10031).

Because the average pore size in paper varies between 400-800 nm, we can suppose that a part of the nanoparticles could have penetrated into the paper structure (Poggi et al. 2010),

unfortunately, the cross-sectional SEM-EDX analysis (Fig. 9) of the samples revealed that during deacidification most of the magnesium compounds were gathered on the paper surface.

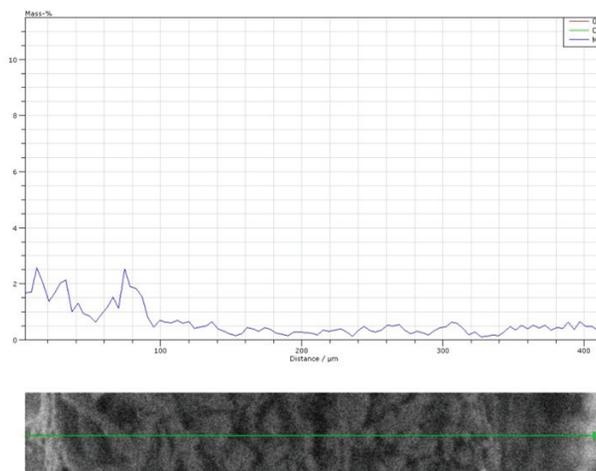


Fig. 9: SEM-EDX analysis of Mg in paper cross-section after deacidifying washing with 0.1 % $Mg(OH)_2$ dispersion in 2-propanol.

This result does not yet entirely exclude the deacidifier's penetration into the internal structures, as the porous nature of the paper's cross section makes an interpretation of such data very difficult. Earlier studies (Wójciak 2015) proved that, when comparing deacidification with standard micro-sized magnesium hydroxide and its nanoparticles, more magnesium in the paper samples was determined in this last case (nanoparticles treatment). This suggests that nanoparticles penetrate more easily into paper pores than larger micro-particles. Studies on the pH of water extracts show that magnesium hydroxide nanoparticles very effectively deacidify paper, yet the question regarding the efficacy of neutralisation remains open. It is connected especially with the deacidification of acid molecules which are present inside the paper structure, i.e. in the fibres wall layers.

$Mg(OH)_2$ as a paper degradation retardant

Protection of DP.

Answers to the question whether an excess of alkali may have a detrimental influence on paper permanence were provided by the analysis of DP after the ageing tests. Data in Tab. 2 confirm an increasing pH of the paper together with a rising concentration of $Mg(OH)_2$ in dispersion. For a 0.1 % concentration the pH reached a relatively high value of 10.54, i.e. more than the minimal value of pH 7.5 which is accepted for permanent papers (e.g. for the ISO 9706 standard). At the same time, the results of the DP determinations show that an increased dosage of alkali did not cause negative consequences, on the contrary, with an increased charge of $Mg(OH)_2$ and higher paper alkalinity, resistance of the samples against ageing degradation also increased. These results are interesting because although deacidification has a rather superficial character, it did not affect the observed increasing trend for DP stabilisation. It is probable that a part of the deacidifier nanoparticles penetrated deeper into the paper structure to give such an effect. However, the fact that magnesium hydroxide effectively stabilises paper may be associated

not only with neutralisation reactions limiting acid hydrolysis but perhaps also with other mechanisms which have not yet been sufficiently recognised. It should be noticed that magnesium compounds introduced into a heterogenic system, e.g. cellulose: liquid (magnesium hydroxide is mainly formed in alkaline media), exhibit the ability to diminish oxidative degradation of cellulose (Lapierre et al. 2000), particularly in terms of the capacity to reduce the hydroxyl radical concentrations (Wójciak et al. 2007).

Similar studies were done on papers covered with iron gall ink. Strongly acidic ink is particularly corrosive and intensifies reactions of cellulose hydrolysis. The iron ions from sulfate salts which are the components of ink are involved in Fenton-type reactions to produce free radicals which contribute to further cellulose degradation. The pH of the paper may influence the catalytic activity of iron ions (Strlič et al. 2003), which are most active at a pH of ca. 8, i.e. at a range close to that obtained after deacidification (Tab. 2). The results of studies on paper samples covered with iron gall ink, subjected to deacidification and followed by artificial ageing confirmed once again that along with an increasing dose of $Mg(OH)_2$ and then of the pH of the paper, the DP of cellulose from the paper samples also increased. Such data were obtained for two experiments differing in the level of deacidification. The first series of experiments concerned papers strongly acidified by iron gall ink in which, despite the relatively small range of neutralisation, the observed increase of DP may be related to an increased pH. In the case of the second experiment, in which the paper samples were deacidified up to four times in order to achieve a pH of 8, no changes of the above-mentioned tendency (the higher the dose of $Mg(OH)_2$, the higher the DP of cellulose after ageing) were observed. These experiments showed that even in the case of highly acidic papers coated with iron gall ink, an increased dose of $Mg(OH)_2$ causes an increased protective effect in the paper. These results were obtained despite the fact that most of the deacidifier was accumulated on the surface of the paper, thus the stabilising effect of magnesium hydroxide is limited and suggests that it mainly concerns its close-surface layers.

Influence of $Mg(OH)_2$ dosage on optical properties.

Although an increased dosage of the deacidifier has a beneficial effect on cellulose's resistance to ageing degradation, it can also cause unfavorable changes in the appearance of the documents. The results in Tab. 3 show a statistically significant increase of ISO Brightness for all of the tested concentrations. It is clear that the nanoparticle deposited on the surface can cover the writing and print, thus limiting its readability. A decrease in the b^* values was also significant and confirmed that magnesium hydroxide causes yellowing of the paper. However, values $\Delta E < 1$ show that the colour change is not noticeable to the average observer. These data are convergent with previous analyses made on real, historical printed papers deacidified with $Mg(OH)_2$ nanoparticles (Wójciak 2014).

Tab. 3: Changes of ISO Brightness, b^* and ΔE values (CIE $L^*a^*b^*$) of papers after deacidification with different charges of $Mg(OH)_2$ nanoparticles; reference - ISO Brightness 85.28 %; Mann-Whitney test for ISO Brightness and b^* measurements before and after deacidification.

$Mg(OH)_2$ concentration (%)				
0.1	0.3	0.6	0.9	1.2
Increase of ISO Brightness after deacidification (%)				
(+) 0.17	(+) 0.35	(+) 0.40	(+) 0.34	(+) 0.58
Mann-Whitney test („Z” and „p” values respectively)				
-3.26; 0.0011	-3.61 0.0011	-4.65 0.0000	-4.09 0.0000	-4.65 0.0000

Decrease of b^* values after deacidification				
(-) 0.05	(-) 0.1	(-) 0.06	(-) 0.04	(-) 0.12
Mann-Whitney test („Z” and „p” values respectively)				
2.5	4.67	4.48	2.13	4.70
0.0124	0.0000	0.0000	0.0000	0.0000
ΔE				
0.1	0.16	0.16	0.14	0.24

Although statistical analysis of the results from Tab. 3 did not confirm significant differences in the optical properties between papers that were non-deacidified and deacidified with various charges of nanoparticles, these relations changed after thermal ageing (Tab. 4).

Tab. 4: Changes of ISO Brightness, ΔE and b^* values (CIE $L^*a^*b^*$) of papers after deacidification with $Mg(OH)_2$ nanoparticles followed by thermal ageing; recto side of paper samples (pH before deacidification 4.45; reference ISO Brightness 85.28 %).

Reference pH 7.36	Concentration of $Mg(OH)_2$ (%)			Acid paper pH 4.55
	0.1	0.6	1.2	
Decrease of ISO Brightness (%)				
(-) 25.35	(-) 16.28	(-) 14.6	(-) 13.13	(-) 26.68
b^*				
10.80	7.62	7.00	6.39	11.32
ΔE				
9.80	5.1	4.1	4.1	9.1

Clearly, neutral and acidified samples yellowed the most intensely (Fig. 10). The multiple comparison tests for all observations also showed significant differences between samples treated with 1.2 and 0.1 % concentrations.

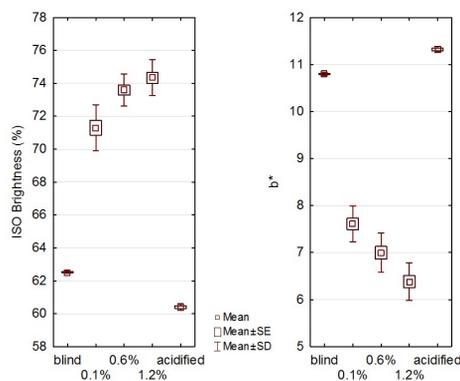


Fig. 10: Box-plot for multiple comparison analysis of paper samples after thermal ageing: blind – neutral reference paper, pH 7.36, acidified – paper with a pH of 4.45, papers acidified and then deacidified with dispersion of $Mg(OH)_2$ having a concentration of 0.1, 0.6 and 1.2 %.

Generally, samples deacidified with higher charges of $Mg(OH)_2$ (0.6-1.2 %) showed a statistically significant smaller loss of ISO Brightness and lower values of coordinate b^* . It should

be stressed that, despite covering the paper surface by magnesium compound particles, differences in the optical properties were so significant that they suggested possible interaction between the magnesium compounds and the cellulose which reduced the formation of new chromophores during thermal ageing. Although the protective effect of deacidification by magnesium hydroxide is obvious, the relatively high results of the ΔE calculations leave open the question regarding to what extent thermal ageing can simulate natural ageing processes.

CONCLUSIONS

1. Studies using the SEM-EDX and XPS methods showed that deacidification with a dispersion of $Mg(OH)_2$ in 2-propanol results in neutralisation of at least a part of the sulfuric acid molecules present in the acidified paper. Microscopic observations indicated that deposits of magnesium compounds accumulated mainly on the surface of the paper, and that the process of deacidification was to a large extent superficial.
2. The introduction of magnesium hydroxide nanoparticles to acid papers protects the cellulose against hydrolytic degradation and depolymerisation. The protective effect of $Mg(OH)_2$ also occurs in the case of paper covered with gall ink containing iron ions. The protective effect of deacidification increases along with an increased dosage of magnesium hydroxide.
3. Deacidification with the use of magnesium hydroxide nanoparticles causes an imperceptible increase of ISO Brightness and yellowing of paper. Deacidification stabilises the changes of cellulose chromophores preventing the yellowing of paper with respect to the thermal ageing tests. This protective effect of deacidification appeared when relatively high concentrations of $Mg(OH)_2$ dispersion, between 0.6 and 1.2 %, were applied.

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