

# Sol–gel synthesis of calcium nanomaterial for paper conservation

**Olga Darčanova\***,

**Aldona Beganskienė,**

**Aivaras Kareiva**

*Department of Inorganic Chemistry,  
Vilnius University,  
Naugarduko St. 24,  
LT-03225 Vilnius, Lithuania*

Nanoparticles of calcium oxide (100 nm), prepared using the sol–gel citrate method, were sonicated for 20 min in water and used for paper deacidification treatment via the Barrow method. For comparison, deacidification was also performed using bulky calcium hydroxide.

Also tested as reagents, were mixtures of the two previously mentioned reagents with the addition of 0.1% gelatin, as well as Bookkeeper alkali material. After thermal accelerated aging at 90 °C for 512 h, all paper samples were investigated by scanning electron microscopy (SEM), infrared (FTIR) and absorbance (UV/Vis) spectroscopy. pH, alkaline reserve (AR), paper sorption and strength properties were determined. The highest value of AR and pH was provided by the calcium nanoparticles treated with gelatin. After artificial aging, the gelatin-treated bulky, nano-sized calcium hydroxide and Bookkeeper alkali material demonstrated an equal decrease in AR and pH. Added gelatin increased the binding of alkali material to paper. Also, measurement of paper strength showed that gelatin treated paper even after aging can resist higher force before breaking. At the same time addition of 0.1% of gelatin did not change paper sorption properties. FTIR and UV/Vis spectra analysis after the artificial aging process confirmed the positive effect of nano-sized calcium hydroxide.

**Key words:** paper, deacidification, calcium nanomaterials, aging, sol–gel synthesis

## INTRODUCTION

Calcium oxide, hydroxide and carbonate have many possible applications – paint, paper industries. Ultra-fine calcium oxide can be used as a catalyst, a toxic-waste remediation agent, an additive in refractory, bactericide, they are widely used as a destructive absorbent for toxic chemical agents, for example, for flue gas desulfurization and pollutant emission control control [1, 2]. Commercially produced calcium carbonate, hydroxide or other derivatives are widely used for paper treatment – deacidification of ancient documents, books, art works, which are slowly degrading due inherent aging of cellulose substrate, technological errors of the past, media, pollution [3].

Using alkali materials, useful life of documents can be extended and processes of degradation can be slowed. Nanoparticles of calcium oxide and hydroxide just started to be used for wall painting conservation. Submicron and smaller particles have very high surface area, so they are very active. Electrostatic forces hold these particles tightly to the surface, also they

are small enough and do not affect layer features. Calcium hydroxide is an excellent deacidifying agent which insures good physicochemical compability with the support even after its transformation into calcium carbonate. It also should work very well as an alkaline reservoir and does not originate any undesirable side products [4]. A specific surface area of smaller size nanoparticles increases exponentially with the decrease of its volume, so the alkaline surface area is available to react with acid groups with superior capacity of neutralization. Also, smaller particles have a better ability to penetrate in the cellulose fiber net, reaching more easily all the thickness of paper, not forming a white glazing film at the surface, which does not affect the appearance of the paper, its readability and / or its aesthetic value.

To obtain calcium hydroxide nanoparticles there are used several methods, such as sonochemical, hydrogen plasma reaction, precipitation, water-in-oil microemulsions. CaO nanoparticles are often produced via thermal treatment (decomposition) of  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$ . CaO nanoparticles could be prepared by the sol–gel method without using any surfactants and complicated tools. Precursors for the sol–gel process are

\* Corresponding author. E-mail: olga.darcanova@chf.vu.lt

simple and completely used during synthesis, there is no need of any purification or washing [1, 5, 6].

The aim of this study was to obtain calcium nanomaterial suitable for paper conservation using the sol–gel method, to perform deacidification of paper and to compare the obtained results with deacidification treatment of currently used systems.

## EXPERIMENTAL

All chemical reagents used in our experiments were of analytical grade and directly used without further treatment. Precursors were mixed by adding 4.77 g of  $\text{Ca}(\text{NO}_3)_2$  dissolved in 20 mL  $\text{H}_2\text{O}$  to 19.30 g of citric acid in 20 mL  $\text{H}_2\text{O}$ . The reaction mixture was evaporated at 60 °C, overnight, respectively. Each time sample was completely powdered. The powder was calcined at 600 °C for 5 h by heating rate of 10 K/min from room temperature. Obtained calcium carbonate was powdered and heated again till 900 °C for 5 h, then additionally for 10 h [6].

Calcium hydroxide nano- $\text{Ca}(\text{OH})_2$  (with a small amount of nano-carbonate) was prepared by the sonication (~20 min). The final product as suspension of 0.1782 M in water was used immediately for paper treatment [2, 6].

To estimate the effect of the obtained material, analogous procedures were accomplished with a solution of commercial bulky 0.0202 M  $\text{Ca}(\text{OH})_2$  (Riedel-de Haën AG), used without further purification or any treatment – as restorers use.

Cotton paper samples (Rotabilo, Carl Roth; 80 g/m<sup>2</sup>, 100% of pure cellulose fibers) were dimensioned with 120 mm × 15 mm. The well known W. J. Barrow two-bath method was used for deacidification treatment [7].

The samples of paper were treated with bulky or nano- $\text{Ca}(\text{OH})_2$  at 24 °C for 5 min. Then the samples were immersed in the second solution (from the same bulky or nano- $\text{Ca}(\text{OH})_2$  bubbled with  $\text{CO}_2$ , l/min, till pH 6.65) and desiccated in 90 °C for 5 min (sample CH or nCH).

Before treatment, the solution-suspension of nano- $\text{Ca}(\text{OH})_2$  was investigated using a Malvern Nano ZS instrument. The size of the obtained particles in water was 170–200 nm and 160–170 nm of the particle prepared from the same solution but with presence of gelatin (0.1 weight %). Two additional sets of samples with gelatin were prepared – one set with commercial bulky and the second set with nano-sized calcium compounds (sample nCHG – cotton paper with nano-sized calcium hydroxide and gelatin, CHG – cotton paper with commercial calcium hydroxide and gelatin).

And the 5th set of paper samples was treated with a Book-keeper (Preservation Technology L. P.) commercial mixture of nanoparticles, designed for paper treatment – samples were sprayed (10 cm distance) and desiccated for 5 min at room temperature, the procedure was repeated 2 times, paper was dried at room temperature (sample CB).

One set of samples was investigated immediately and compared with other set – after accelerated aging at 90 °C for 512 h. Artificial aging tests give us relative results, which help us to compare the stability of paper samples with and without the

studied deacidification treatments. Comparison between samples before / after deacidification and before / after aging tests was made. Cotton paper with any additives was also aged and investigated (sample C).

The pH value of the cold water extract was measured according to the international standard ISO procedure [8], measurements were performed using a Mettler Toledo pH meter MP 220. The alkaline reserve (AR) was also determinate according to the standard ISO method [9].

XRD analyses of the obtained materials were performed using Benchtop XRD MiniFlex II, Rigaku. The surface morphology of the paper samples (analysis SEM/EDX) was studied using Hitachi TM3000.

IR spectroscopy was used for identification and changing of the characteristic functional groups of cellulose. Infrared spectra were obtained by a FTIR spectrophotometer, model Perkin Elmer Spektrum Frontier with ATR accessory. All spectra were recorded at 4 cm<sup>-1</sup> resolution in an interval of 600–4 000 cm<sup>-1</sup> and 20 scans were accumulated before Fourier transformation.

UV/Vis diffuse reflectance spectra were measured at room temperature by using a Lamda 35 Perkin Elmer spectrophotometer equipped with a  $\text{BaSO}_4$  coated integrating sphere and normalized to a Labsphere reflectance standard. All spectra were taken in an interval of 200–1100 nm, measured in a speed of 120 nm/min, an interval of 1 nm, and duration of cycle 1 s. The UV/Vis spectra are shown as pseudo-absorbance calculated from reflectance though the Kubelka-Munk transformation. The sorption properties of paper were evaluated using KSV Instruments LTD (MODEL CAM 200), the drop of 8  $\mu\text{L}$  of distilled water was placed on the paper surface and 10 pictures each 0.033 s were recorded.

## RESULTS AND DISCUSSION

Calcium oxide nanoparticles were prepared using citric acid as an organic additive – emulsifier, the procedure is known as the so-called sol–gel citrate method. Formation of citrate complexes effectively keeps the constituent metal cation dispersed homogeneously and makes formation of nanoparticles of carbonate and then oxide easier [10].

The obtained materials were investigated by the X-ray diffraction analysis (Fig. 1).

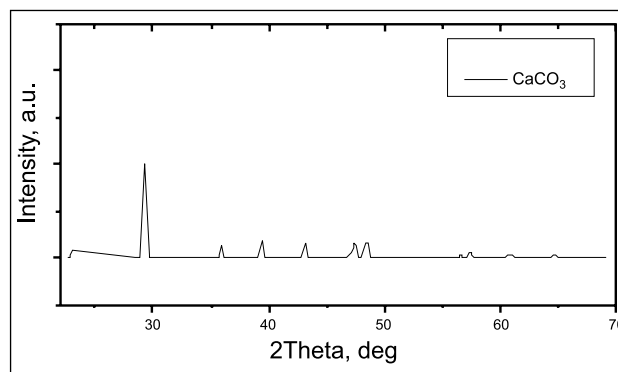


Fig. 1. XRD pattern of  $\text{CaCO}_3$  obtained by sol–gel method

The XRD pattern data confirmed that after calcination at 600 °C for 5 h the obtained product is pure calcium carbonate as the calcite phase (PDF 00-088-1808).

Figure 2 shows typical scanning electron micrographs of  $\text{CaCO}_3$  obtained by the sol-gel method. As seen, the obtained particles tend to agglomeration, but on examining the micrograph closely some spherical particles with  $\sim 200$  nm size can also be noticed.

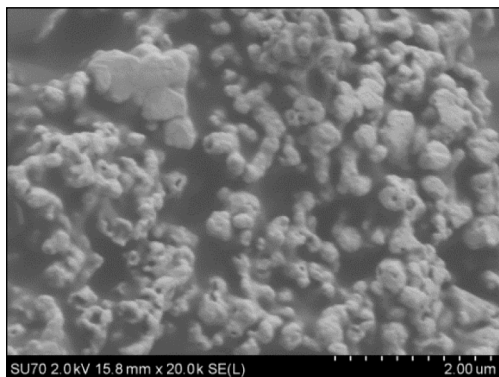


Fig. 2. SEM image of  $\text{CaCO}_3$  obtained by sol-gel method

Then this material was calcined at 900 °C for 5 h [6]. The XRD analysis showed that the obtained material was not pure  $\text{CaO}$ , so grinding and then heating of powder for 10 h was performed again. The obtained material was pure  $\text{CaO}$  and corresponds to PDF:00-43-1001, as the lime phase (Fig. 3).

In Fig. 4 the SEM image of the obtained material is demonstrated, the particle size is about 100 nm. They tend to agglomeration, but on examining the micrograph closely the form of particles is spherical and irregular hexagonal.

The obtained material was used for further paper treatment via the Barrow method. At first, the influence of deacidification treatment after accelerating aging on the chemical properties of paper samples was investigated, monitoring the changes in pH of the cold extract and alkaline reserve. Deacidification denotes the treating of the paper-based object to neutralize its acidic content, with the objective of prolong-

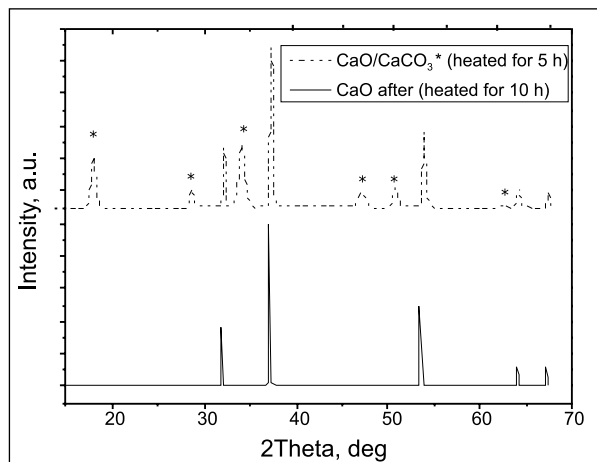


Fig. 3. XRD pattern of  $\text{CaO}$  obtained by sol-gel method

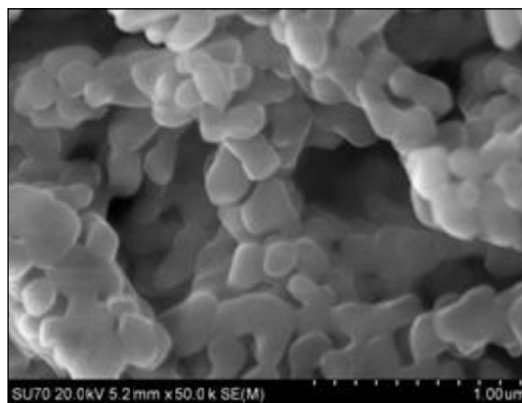


Fig. 4. SEM image of obtained  $\text{CaO}$  particles

ing the object's useful life. Most deacidification measures also provide a reserve of alkalinity to neutralize acids, that may be generated in the future either from within the paper itself or by introduction from its storage environment [3]. The conditional dimension of the alkali reserve is  $\text{OH}^-$  mol/kg and 0.2 of it corresponds to 1% of  $\text{CaCO}_3$  in the substance.

To evaluate the effect of paper samples treatment with different alkali materials and procedures, acidity in pH and the alkaline reserve (AR) was determined. The results are presented in Fig. 6.

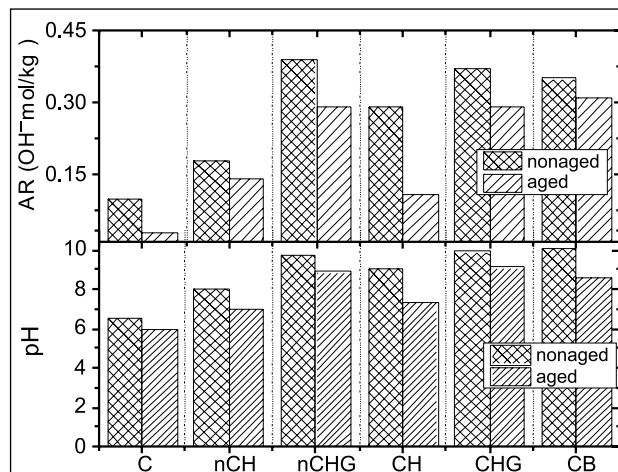


Fig. 5. AR and pH results of pure cotton (C) and paper samples treated: nano- $\text{Ca}(\text{OH})_2$  (nCH), nano- $\text{Ca}(\text{OH})_2$  with gelatin (nCHG), commercial  $\text{Ca}(\text{OH})_2$  (CH), commercial  $\text{Ca}(\text{OH})_2$  with gelatin (CHG) and cotton paper with Bookkeeper (CB)

After treatment with different deacidification reagents and procedures, pH value of all samples increased. pH of Bookkeeper sprayed samples increased till 10.7 and after aging for 512 h remains high enough – 8.56. Bookkeeper creates the alkaline reserve (AR) in paper of 0.35 relative units, after aging this value changes slightly – 0.31. Commercial  $\text{Ca}(\text{OH})_2$  creates 0.29 of AR, but after aging it decreased up to 0.11. The addition of gelatin (0.1 weight %) to commercial  $\text{Ca}(\text{OH})_2$  solution increased AR to before and after aging the residue of AR was 0.29. pH of the same samples was 8.99 before and 7.30 after aging

and after addition of gelatin pH increased up to 9.89. Very similar pH values of the samples after treatment using nano-sized calcium materials prepared by the sol-gel method were measured. The alkaline reserve provided by nano- $(\text{CaOH})_2$  was the lowest – 0.18 OH<sup>-</sup> mol/kg, but if we compare it with commercial  $\text{Ca}(\text{OH})_2$  – after aging the alkaline reserve remained higher for 0.03 points and when gelatin was added, values were equal.

Gelatin increases the link of alkali material to paper fibers, so the effect on paper strength was investigated. Tensile strength is indicative of fiber strength, fiber bonding and fiber length. Fiber length and coarseness also influence the tensile strength of paper. The tensile strength of paper is the maximum force per unit that a paper strip can resist before breaking when applying load in the direction parallel to the length of a strip. Also, it should be mentioned that the paper which was used in this study had no specific orientation of the fibers (machine and cross direction).

The strength of paper after aging decreased by 5.6% (Table). But deacidifying treatment decreased it even more – 13–20%. Water treatment reduced the bond of paper fibers and released them. The nano- $\text{Ca}(\text{OH})_2$  changed this paper characteristic the least. After gelatin was added, the values of breaking force were only slightly smaller than non-alkali-treated paper. So, the gelatin acted like a binding material. The lowest value of break force was detected after Bookkeeper was used, probably additives used for this commercial product stabilization affected and reduced the paper strength.

Sorption capabilities of moisture, water and dye are very important properties of paper. The molecular and intermo-

lecular structure of fibers had influence on sorption properties – degree of crystallinity, amorphous and void regions. The bigger adsorption is the bigger the swelling of the moisture is, as a result of it – volume of fibers increases. The sorption properties of paper can be evaluated through contact angle measurements – the angle of water droplet deposited onto its surface. If there is no swelling of water and contact angle is higher than 90°, material can be defined as hydrophobic [11, 12].

The contact angle measurement (CAM) of all samples, pure and treated paper, was performed before and after aging. The data showed that paper properties remained unchanged – swelling of water was very similar before and after deacidification, and also before and after accelerated aging. In all cases drop was swelled faster than in 1 second (contact angle did not comprise  $\theta = 0^\circ$ ) and to illustrate the obtained results data on untreated paper (C) and paper with nano- $\text{Ca}(\text{OH})_2$  with addition of gelatin and after artificial aging (nCHG) are presented in Fig. 6.

The results show that addition of synthesized  $\text{Ca}(\text{OH})_2$  and 0.1% gelatin did not change the sorption properties of paper, even after aging they remain similar.

The study of paper surface morphology was performed using a scanning electron microscope. The SEM images (Fig. 7) showed that the surface of paper was not affected after treatment with alkali material. Particles of nano- $(\text{CaOH})_2$  bind to paper fibers better than particles of bulky- $\text{Ca}(\text{OH})_2$ . It can be seen that particles bind to paper fibers even better after gelatin was applied.

Typically, paper degradation is monitored by changing the chemical, mechanical or physical properties, such as pH, tensile strength, etc. But these parameters provide only macroscopic information about the paper condition. Vibrational and absorption spectroscopy is often used to resolve the cellulose structure or crystalline phase, hydrogen bond network. Application of in situ FTIR measurements to directly look into the changes of cellulose structure during the degradation is possible [13]. So, the functional group changing of paper and alkaline material was studied by infrared and UV/Vis absorbance spectroscopy.

Characteristic bands of cellulose functional groups that appear after aging can be observed in the regions of valence

Table. Break force measurement data for treated paper samples

Sample	Break force, N/mm <sup>2</sup>	
	Nonaged	Aged
Paper (C)	41.4	39.1
Paper + Bookkeeper (CB)	24.5	20.2
Paper + $\text{Ca}(\text{OH})_2$ (CH)	34.4	33.1
Paper + $\text{Ca}(\text{OH})_2$ + gelatin (CHG)	39.1	35.1
Paper + nano- $\text{Ca}(\text{OH})_2$ (nCH)	35.6	35.2
Paper + nano- $\text{Ca}(\text{OH})_2$ + gelatin (nCHG)	39.9	36.2

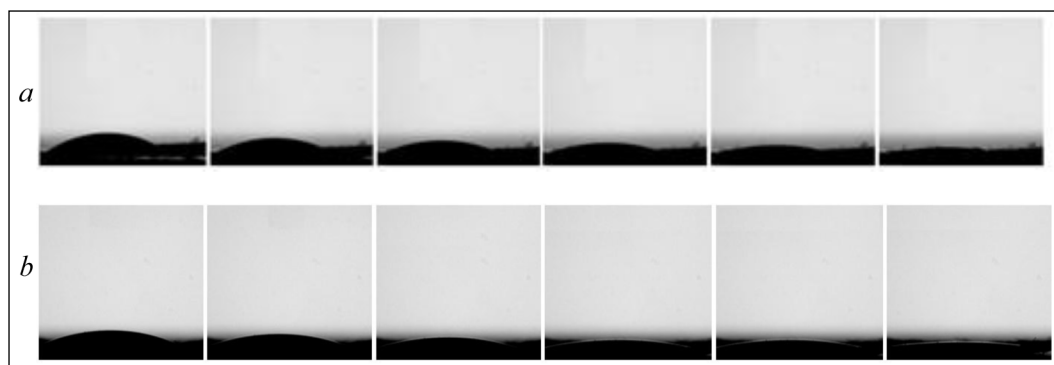


Fig. 6. Pictures, captured each 0.033 s (till 0.198 s) after drop placed on (a) untreated cotton paper (C); (b) cotton paper treated with nano- $\text{Ca}(\text{OH})_2$  with addition of gelatin after artificial aging (nCHG)

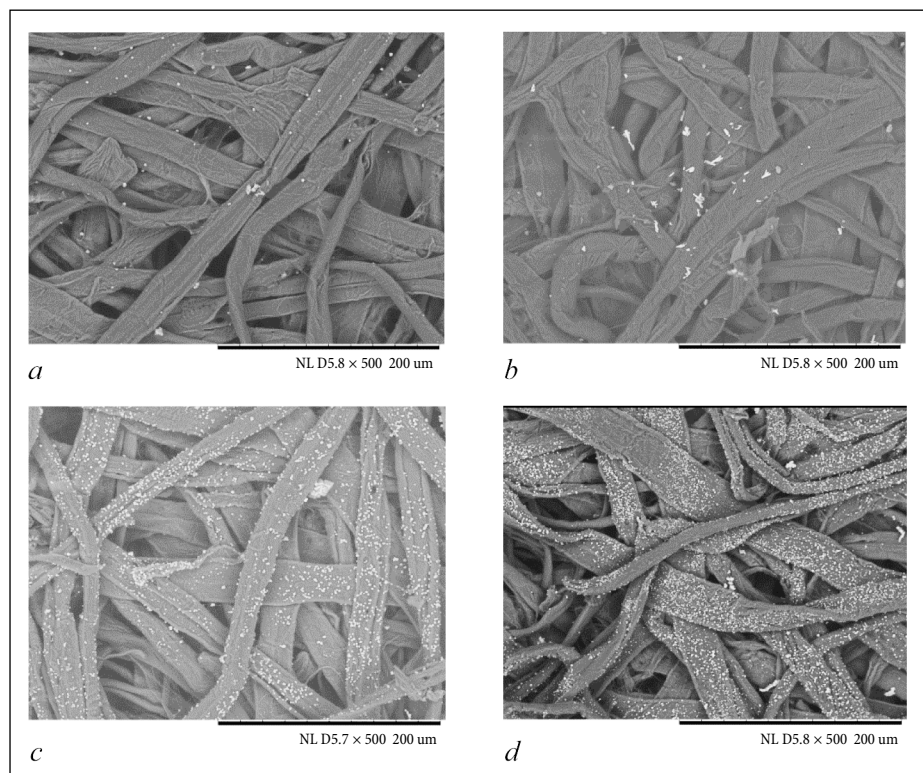


Fig. 7. SEM picture of aged paper with (a) bulky  $\text{Ca(OH)}_2$ , (b) bulky  $\text{Ca(OH)}_2$  and gelatin, (c) nano- $\text{Ca(OH)}_2$ , (d) nano- $\text{Ca(OH)}_2$  and gelatin

vibrations (Fig. 8):  $3\,600\text{--}3\,300\text{ cm}^{-1}$  – corresponding to the OH groups,  $3\,000\text{--}2\,800\text{ cm}^{-1}$  – CH groups from  $-\text{CH}_3$ ,  $-\text{CH}_2-$  and CH;  $1\,760\text{--}1\,650\text{ cm}^{-1}$  – carbonylic and carboxylic groups  $\text{C}=\text{O}$ ;  $1\,500\text{--}1\,200\text{ cm}^{-1}$  – mainly deformations of the vibrations of  $-\text{CH}_2\text{--OH}$  primary alcoholic groups appear along with deformations of the C–O and CH links;  $1\,200\text{--}900\text{ cm}^{-1}$  – C–O, C–C links of the pyranose cycles ( $1\,050\text{ cm}^{-1}$ );  $900\text{--}400\text{ cm}^{-1}$  – deformation bands of the  $-\text{CH}_2\text{--OH}$ ,  $-\text{CH--OH}$  groups and pyranose cycles [14]. Spectral peaks at  $3\,450\text{ cm}^{-1}$  and  $1\,640\text{ cm}^{-1}$  assigned to OH vibration of water are observed. Zone of  $2\,350\text{ cm}^{-1}$  is characteristic of  $\text{CO}_2$  in environment. But the actual peak height

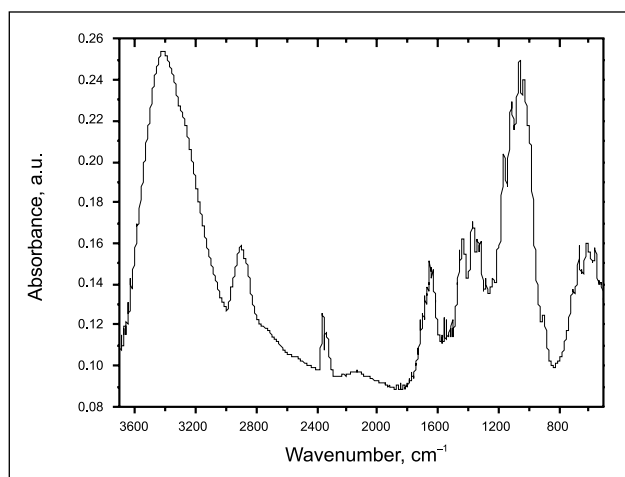


Fig. 8. FTIR spectra of cellulose paper

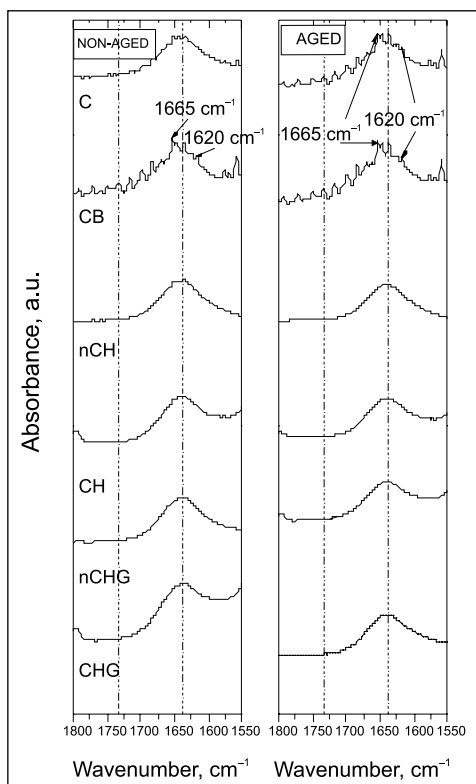
can vary slightly with position on the surface of the sample, due to local inhomogeneity of the surface of paper [13, 15].

All FTIR spectra (in Fig. 9) were normalized at the area of the CH vibration band between  $2\,800$  and  $3\,000\text{ cm}^{-1}$ , since the band at around  $2\,900\text{ cm}^{-1}$ , whose main intensity comes from CH stretching vibrations, does not change with time [13, 16].

In general, after aging, the carbonyl / carboxyl peak can form, and increasing of absorbance in the FTIR spectrum at the region  $1\,600\text{--}1\,700\text{ cm}^{-1}$  can be observed in cotton paper. However, the changes can be masked by the presence of free water in the paper near  $1\,640\text{--}1\,700\text{ cm}^{-1}$ . Presence of enolic groups can be observed at  $1\,665$  and  $1\,620\text{ cm}^{-1}$  and both bands are observed in the aged cotton and cotton treated with Bookkeeper before and after aging.

The application of Bookkeeper causes deceleration of carbonyl formation (the decrease of spectral band intensity at  $\sim 1\,735\text{ cm}^{-1}$ ). And more intensive formation of carboxylates was observed (the increase of band  $\sim 1\,638\text{ cm}^{-1}$ ) [17]. The spectra of the sample treated with nano- and bulky  $\text{Ca(OH)}_2$ , both show reduction of the same band intensity ( $1\,735$  and  $1\,638\text{ cm}^{-1}$ ). After thermal aging a small increase of  $1\,735\text{ cm}^{-1}$  (that corresponds to paper degradation / hydrolysis) can be observed when commercial  $\text{Ca(OH)}_2$  is used, while the intensity of the same bands when nano- $\text{Ca(OH)}_2$  was used did not change. It means that the proved reserve of alkali materials is still sufficient.

Addition of 0.1% of gelatin has a positive effect on the particles binding to cellulose, that is why we can see small

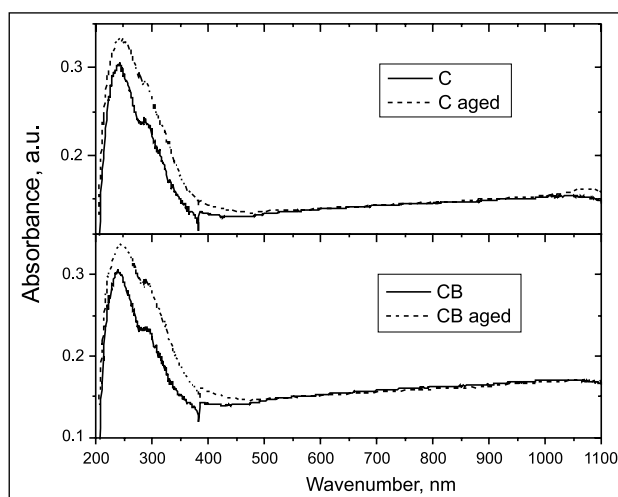


**Fig. 9.** FTIR spectra of aged and non-aged pure cotton (C) and paper samples treated: nano- $\text{Ca}(\text{OH})_2$  (nCH), nano- $\text{Ca}(\text{OH})_2$  with gelatin (nCHG), commercial  $\text{Ca}(\text{OH})_2$  (CH), commercial  $\text{Ca}(\text{OH})_2$  with gelatin (CHG) and cotton paper with Bookkeeper (CB)

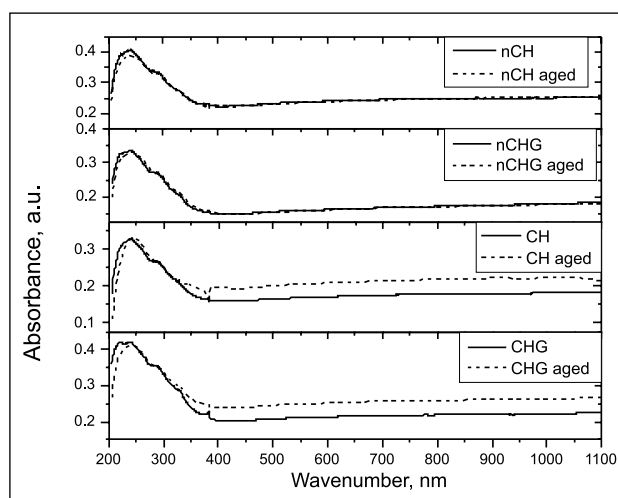
decreasing of the peak intensity  $\sim 1735\text{ cm}^{-1}$ , but we must be careful with our interpretation in interval  $1660\text{--}1630\text{ cm}^{-1}$  and keep in mind that the spectra in this range can overlap with the gelatin amide peak.

The UV/Vis absorbance spectra of paper and treated paper samples are presented in Figs. 10 and 11. Degradation through chemical changes of the macromolecules could have two consequences: loss of physical properties and change in appearance. During paper aging, especially oxidative degradation, the chromophores such as CO, C=C or C=N bonds are formed, they can be observed in the UV/Vis region and they affect the growth of wavelength portion of the visible spectrum ( $\lambda < 430\text{ nm}$ ). Yellowing through absorption of the temperature treated paper can be based on absorbance increase at about  $420\text{ nm}$  [18, 19]. Unaged paper shows two distinct maxima at  $228$  and  $282\text{ nm}$ . Upon aging, these two maxima grow the overall intensity in the pseudoabsorbance in the UV/Vis increases and a new shoulder around  $360\text{ nm}$  emerges [16]. The UV/Vis spectra of samples are presented in Figs. 10 and 11.

This changing can be observed in Fig. 10. After aging of the cotton paper and paper treated with Bookkeeper the overall intensity in this region increases. In Fig. 11 the spectra of paper treated with nano-calcium hydroxide are very similar to the spectra before thermal treatment. And the spectra of paper treated with commercial calcium hydrox-



**Fig. 10.** UV/Vis spectra of cotton paper and paper with Bookkeeper (before and after aging)



**Fig. 11.** UV/Vis spectra of aged and non-aged nano- $\text{Ca}(\text{OH})_2$  (nCH), nano- $\text{Ca}(\text{OH})_2$  with gelatin (nCHG), commercial  $\text{Ca}(\text{OH})_2$  (CH) and commercial  $\text{Ca}(\text{OH})_2$  with gelatin (CHG)

ide or with gelatin show the overall increase of absorbance in all spectral region.

## CONCLUSIONS

Pure calcium oxide nanoparticles ( $100\text{ nm}$ ) obtained using the sol-gel citrate method are suitable for paper conservation via the Barrow two-bath method. The treated paper had a high enough pH and contained an alkaline reserve. Addition of  $0.1\%$  gelatin to the bulky and nano- $\text{Ca}(\text{OH})_2$  deacidification systems increases pH, alkaline reserve and paper strength. At the same time the use of gelatin and alkali treatments did not change paper fiber morphology and sorption properties. FTIR and UV/Vis spectra analysis shows that carboxylic species decrease after deacidification treatment with a nano- $(\text{CaOH})_2$  gelatin mixture.

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Olga Darčanova, Aldona Beganskienė, Aivaras Kareiva

### KALCIO NANODALELIŲ SINTEZĖ ZOLIŲ-GELIŲ METODU KONSERVUOTI POPIERIŲ

#### Santrauka

Kalcio oksido dalelės (100 nm), pagamintos zolių-gelių metodu, buvo sonifikuotos ir naudotos popieriui šarmininti pagal gerai žinomą Barou metodą. Popierius taip pat buvo šarminintas naudojant komercinį kalcio hidroksidą. Ištirti tokios pačios sudėties mišiniai, papildomai įdėjus 0,1 % želatinos.

Po terminio sendinimo 90 °C 512 val. bandiniai buvo ištirti skenuojančių elektronų mikroskopu (SEM), įrašyti infraraudonosios spektroskopijos (FTIR) ir sugerties UV/reg spektrai, nustatytas popieriaus rūgštingumas (pH) ir šarminė atsarga (ŠA). Po terminio sendinimo stebimas pH ir ŠA sumažėjimas. Mėginiai papildomai veikti želatina tolygiau pasidengė šarminimo medžiaga, o popieriaus mechaninių savybių (tempimo) testas parodė, kad šie mėginiai yra tvirčiau. FTIR ir UV/reg spektrinė analizė patvirtino teigiamą nanokalcio hidroksido poveikį.