**Tensile and Stretch of Paper Filled with Bactericidal Zeolites**

*Abstract.* The purpose of present work was to study tensile and stretch of paper prepared with the use of bactericide zeolite fillers containing up to 130 mg/g of silver, 72 mg/g of copper, and 58 mg/g of zinc, prepared by ion exchange reactions using heulandite-clinoptilolite from the Rkoni.
plot of the Tedzami deposit, Eastern Georgia. Filled papers with zeolite content up to 4 g/m² and bactericidal activity confirmed by the colony forming unit assay were manufactured on the production lines of the GPM enterprise (Tbilisi, Georgia). The measured tensile strength and percentage elongation of filled paper depend on the nature of the filler and its metal content; the introduction of pure zeolite filler reduces the tensile and stretch of the paper, but fillers containing silver and copper increase the tensile strength. Accelerated aging results in lower tensile and stretch, but zeolite fillers generally make the paper more resistant to aging.

**Keywords:** zeolite paper filler, silver, copper, zinc, tensile strength, stretch, accelerated aging

**Introduction**

Paper is a complex composite material made up of a combination of biological, synthetic, and inorganic materials. Components include wood pulp and other wood components or other fibers and fines, inorganic (mineral) and organic fillers, natural and synthetic polymers for sizing, retention and strength, as well as other additives to meet specific product or process requirements. Zeolites have been used in papermaking since the 1960s as fillers not only for filter papers [1], but primarily to improve optical properties of paper, its bulk and printability, as well as to increase retention at the wet end [2].

The first experimental results showed that the use of clinoptilolite as filler for machine glazed paper, writing paper, frisket paper, and newsprint paper is feasible, and the quality of types of paper with clinoptilolite filler fully meets the requirements for the adopted product [3].

Retention of the individual components in appropriate amounts is critical to the properties and quality of the paper sheet as well as to minimize environmental pollution and production cost. A microparticle retention aid for use in papermaking containing a high performance purified natural zeolite pigment has been disclosed [4]. According to the inventors, the use of zeolite facilitates manufacture of papers with improved quality and economy: when used as a filler, the zeolite pigment is readily retained and eliminates print-through in uncoated papers; the zeolite pigment is low in abrasion and provides an improved coefficient of friction.

Zeolites are also used to control organic contaminants in fibers and to reduce stickiness in paper mill furnish formed with recycled fibers, as well as for pitch control in paper mill furnish formed with virgin fibers [5].
The production of zeolites enriched with bioactive metals was patented under the name “Antibiotic zeolite” first in Japan (1986) and then in Europe [6], but a detailed study of the properties and bactericidal activity of such materials began only in the 21st century (a brief overview of publications is given in our article [7]). As a result of studies of silver-, copper- and zinc-containing synthetic and natural zeolites, it was found that the silver-containing samples are the most active, but the disadvantages of the use of silver ions have been noted – silver is an expensive metal, and Ag⁺ is not stable in aqueous solutions, tends to be reduced to Ag⁰ and reacts with sulfate and other anions forming insoluble salts [8], so in some cases the benefits of silver ions are not so obvious. In most studies applying natural zeolites for the preparation of bactericidal materials, heulandite-clinoptilolite of various origins, purity (zeolite phase content), chemical composition and properties was used, and the results on the content of bioactive metals in enriched clinoptilolites and their bactericidal activity are contradictory.

Research on the incorporation of germicidal zeolite fillers into paper has only recently begun [9-11], although it has previously been proposed [12] to combine zeolite formulations with various materials used in manufacturing medical devices, surfaces, textiles, or household items with antimicrobial properties required.

We used heulandite-clinoptilolite from the Rkoni plot of the Tedzami deposit, Eastern Georgia, as a raw material for obtaining silver-, copper-, and zinc-containing microporous materials [7] according to the previously described method [13,14] using ion-exchange reactions between mechanically mixed preliminary acid-treated zeolite microcrystals and a salt of a corresponding bioactive metal in the solid phase followed by washing with distilled water. Synthesized in such way biometal-containing adsorbent-ion-exchangers were characterized by X-ray energy dispersion spectra, powder X-ray diffraction patterns, and Fourier transform infra-red spectra. Obtained materials remain the zeolite crystal structure, contain over 130 mg/g of silver, 70 mg/g of copper, and 55 mg/g of zinc, show bacteriostatic activity towards gram-negative bacterium Escherichia coli, gram-positive bacteria Staphylococcus aureus and Bacillus subtilis, fungal pathogenic yeast Candida albicans, and a fungus Aspergillus niger, their mixtures exhibit a synergistic effect – the silver form with
additives of copper and zinc forms is most active against staphylococcus, and against other microorganisms, mixtures of copper and zinc forms are most effective.

The resulting materials were used as fillers for the manufacture of paper with bactericidal properties, and the colony forming unit (CFU) assay showed the activity of all metal-containing samples against staphylococcus and all samples containing silver and zinc against E. coli [11]. The introduction of zeolite fillers containing divalent metals copper and zinc causes a significant change in surface properties of paper, and samples with a certain copper content become absolutely waterproof. A preliminary study of the mechanical properties of filled paper showed that the introduction of zeolite fillers leads to an increase in the basis weight (grammage), thickness (caliper) and density of the paper, as well as to some decrease in the tensile strength in the machine direction.

The purpose of this work was to thoroughly study the tensile strength (indicative of the strength derived from factors such as fiber strength, fiber length, and bonding) and stretch (percentage elongation, indicative of the ability of paper to conform to a desired contour, or to survive non-uniform tensile stress) of filled paper and take into account their possible changes in the aging process of the paper. The investigated paper is used for the production of three-layer corrugated cardboard and boxes based on it; boxes are used for storing and transporting food and other products, their aging occurs under various conditions, and knowledge about the change in the mechanical properties of the box material is of great practical interest.

**Experimental**

Zeolite-filled paper samples were obtained on the production line of GPM (Tbilisi), the largest manufacturer in Georgia of cardboard and boxes for wine and agricultural products. At one of its factories, the company produces paper from recycled waste, and from this paper it makes three-layer corrugated cardboard.

The introduction of fillers on the surface of the paper was carried out during coating, by adding a zeolite suspension in a binder of cooked starch. It has been found that it is optimal to add 140 g (in terms of the initial zeolite matrix $\text{H}^+(\text{H}_2\text{O})_3[\text{AlSi}_{13.6}\text{O}_{9.2}]$) of zeolite filler and spread it over approx. 40 square meters of paper web entering the reel drum (see Fig. 1).
Fig. 1. Scheme of introducing zeolite fillers into paper

The chemical composition of prepared paper samples was determined on the basis of X-ray energy-dispersive spectra obtained on an X-Max 20 analyzer (Oxford Instruments, UK) spectra [11], results are shown in Table 1.

The basis weight (BW, grammage) of the paper was determined on an electronic analytical balance (FA 2204N, JOAN Lab, China); caliper (C, thickness) was measured with a micrometer as the perpendicular distance between two circular plane parallel surfaces under a pressure of 1 kg/cm²; the density and bulk (weight per unit volume) of the papers were calculated from the measured grammage and caliper, results are shown in Table 2.

**Table 1**

| Sample            | Filler content, g/m² | Bioactive metal content, mg/g |
|-------------------|----------------------|-------------------------------|
|                   |                      | Ag   | Cu   | Zn   |
| P                 | 0                    | 0    | 0    | 0    |
| P-HCR             | 3.5±0.5              | 0    | 0    | 0    |
| P-AgHCR           | 4.0±0.6              | 3.0±0.5 | 0    | 0    |
| P-CuHCR₁          | 3.7±0.6              | 0    | 1.5±0.25 | 0    |
| P-CuHCR₂          | 3.8±0.6              | 0    | 1.6±0.25 | 0    |
| P-ZnHCR₁          | 3.6±0.6              | 0    | 0    | 0.75±0.11 |
| P-ZnHCR₂          | 3.7±0.6              | 0    | 0    | 1.4±0.2 |
| P-(½Cu+½Zn)HCR    | 3.7±0.6              | 0    | 0.8±0.12 | 0.7±0.1 |
Accelerated aging of paper [15] was carried out for 72 hours in an oven at a temperature of 90-100°C and a relative humidity of 25 and 65%. Relative weight loss is 1.8-2.2% and 2.7-3.3% for paper samples aged at low and high relative humidity, respectively.

Before the experiments, samples of native and aged paper were conditioned at a temperature of 20-25°C and a relative humidity of 25-30%; the samples were kept until they reached an equilibrium moisture content, which is considered to be achieved if, after two successive weighings of the sample, carried out after 1 hour, the last mass differs from the previous one by no more than 0.25%.

The tensile force (F, the maximum tensile force developed in a test specimen before rupture) and stretch (S, the maximum tensile strain developed in the test specimen before rupture) of the paper strips (25 mm x 150 mm) were measured on a Universal Testing Machine (Hongtuo, China) at the rate of separation of jaws 25 ± 5 mm/min, measurements have been carried out in machine direction (MD, the direction of the paper web which is running on the machine) and in cross direction (CD, the direction, which is perpendicular to the paper sheet that is running on the machine during paper making).

The tensile strength (TS, the maximum tensile force F developed in a test specimen before rupture per unit width W of test specimen) of native and aged paper samples was calculated as $TS(kN/m) = 10^{-3} \cdot F(N)/W(m)$, see Tables 3 and 4, which also show the relative changes from ordinary and aged paper samples.
Taking into account different paper caliper in samples with different fillers (Table 2), the tensile strength limit (σ, the ratio of the force F causing rupture of the test specimen to the cross-sectional area WC of test specimen) was calculated as 

\[ \sigma = 10^{-6} F(N)/W(m)C(m) \]

see Fig. 3.

The breaking length (BL, the calculated limiting length of a strip of uniform width, beyond which, if such a strip were suspended by one end, it would break of its own weight) was calculated as 

\[ BL(km) = 102TS(kN/m)/BW(g/m^2) \]

and tensile index TI as 

\[ TI(Nm/g) = 1000TS(kN/m)/BW(g/m^2) \]

respectively. 

The stretch (percentage elongation) was calculated as the ratio of the increase in length of the test specimen ΔL to the original test span L: 

\[ S(\%) = 100\% \Delta L(m)/L(m) \]

Results & Discussion

The ordinary GMP paper P has approx. doubled tensile in the machine direction MD compared to the cross direction CD, which is typical of cylinder-machines. The introduction of pure HCR zeolite filler lowers tensile strength by about 20% in both directions equally maintaining the same TSMD/TS_CD ratio in the corresponding P-HCR paper, but metal-containing fillers affect tensile strength differently (see Table 3). Thus, papers containing silver and copper, P-AgHCR and P-CuHCR₁, respectively, and paper with mixed filler P-(½Cu+½Zn)HCR have a higher tensile strength, but paper with a high copper content P-CuHCR₂ has a low tensile strength, especially in the cross direction; zinc-containing paper P-ZnHCR₁ has a lower tensile strength in the machine direction and an increased tensile strength in the cross direction.

The strength of paper is determined by the following factors in combination: (1) the strength of the individual fibers of the stock, (2) the average length of the fiber, (3) the interfiber bonding ability of the fiber, and (4) the structure and formation of the sheet. According to the data of optical (AmScope T690C-PL-10M Digital Trinocular Compound Microscope) and scanning electron (Jeol JSM6510LV) microscopy, the average fiber diameter is 7-12 microns, the maximum is up to 60 microns, the maximum fiber length is up to 2 mm, and these strength indicators do not change when fillers are added to the paper.
The formation of the paper sheet depends on the parameters of the cylinder-machine and the conditions of papermaking, which are the same for ordinary paper and filled paper, so the structure of the paper and fiber bonding are the main reasons for the changes in tensile strength in filled paper.

According to the SEM data (see Fig. 2), the microscopic structure of the paper does not depend on the introduction of zeolite fillers, although this cannot exclude the possibility of some disorientation of the fibers relative to the machine direction, since some of the fibers lie in the cross direction.

Fig. 2. SEM images of paper samples, red arrows show the machine direction
Accelerated aging of ordinary paper P leads to a decrease in tensile strength mainly in the machine direction, and the $\frac{TS_{MD}}{TS_{CD}}$ ratio decreases (see Table 4). The same happens with most papers containing zeolite fillers, for example, aged paper P-CuHCR₁ becomes “square” ($\frac{TS_{MD}}{TS_{CD}}=1$), but silver paper and paper with a mixture of fillers P-(¾Zn+ ¼Cu)HCR show the opposite effect – tensile strength mainly decreases in the cross direction, and the $\frac{TS_{MD}}{TS_{CD}}$ ratio increases.

Table 4

| Sample                | Tensile Strength, kN/m | $\frac{TS_{MD}}{TS_{CD}}$ | Relative change from samples |
|-----------------------|------------------------|---------------------------|-----------------------------|
|                       | MD         | CD         | Ordinary | Aged | MD         | CD         | Ordinary | Aged |
| P                     | 4.17       | 2.97       | 1.40      | 0.74 | 0.94       |            |           |       |
| P-HCR                 | 4.65       | 2.72       | 1.71      | 0.82 | 0.86       | 1.12       | 1.01      | 1.52 | 1.07 |
| P-AgHCR               | 6.32       | 3.19       | 1.98      | 1.12 | 1.01       | 1.52       | 1.01      | 1.52 | 1.07 |
| P-CuHCR₁              | 3.27       | 3.26       | 1.00      | 0.58 | 1.03       | 0.78       | 1.10      |       |
| P-CuHCR₂              | 3.97       | 2.64       | 1.50      | 0.70 | 0.83       | 0.95       | 0.89      |       |
| P-ZnHCR₁              | 3.18       | 2.32       | 1.37      | 0.56 | 0.73       | 0.76       | 0.78      |       |
| P-ZnHCR₂              | 3.85       | 2.44       | 1.58      | 0.68 | 0.77       | 0.92       | 0.82      |       |
| P-(¾Cu+½Zn)HCR        | 2.90       | 2.20       | 1.32      | 0.51 | 0.70       | 0.70       | 0.74      |       |
| P-(½Cu+½Zn)HCR        | 5.51       | 2.67       | 2.06      | 0.97 | 0.84       | 1.32       | 0.90      |       |

The tensile changes are clearly visible in Fig. 3, showing the tensile strength limit $\sigma$ for native and aged paper.

Fig. 3. Diagram of tensile strength limit for native and aged paper
The tensile strength limit graph (Fig. 3) as well as the calculated breaking length (Table 5) and the tensile index (Fig. 4) show the maximum values in both directions for copper paper P-CuHCR₁.

**Table 4**

| Sample                  | Native paper | Aged paper |
|-------------------------|--------------|------------|
|                         | MD  | CD  | MD  | CD  |
| P                       | 3.82| 2.14| 2.82| 2.01|
| P-HCR                   | 2.85| 1.59| 2.86| 1.68|
| P-AgHCR                 | 3.56| 1.92| 3.68| 1.86|
| P-CuHCR₁                | 4.25| 2.38| 2.14| 2.13|
| P-CuHCR₂                | 3.04| 1.41| 2.41| 1.60|
| P-ZnHCR₁                | 3.50| 2.34| 2.24| 1.63|
| P-ZnHCR₂                | 3.03| 1.69| 2.53| 1.61|
| P-(½Cu+½Zn)HCR          | 3.23| 1.73| 1.85| 1.40|
| P-(½Zn+¼Cu)HCR          | 3.12| 1.73| 3.51| 1.70|

Fig. 4. *Tensile index of native and aged paper*

Stretch is indicative of the ability of paper to conform to a desired contour, or to survive nonuniform tensile stress, it is considered important in all papers, but is of particular importance in papers where stress-strain properties are being modified or controlled [16]. The percentage elongation of ordinary paper in the cross direction is greater than in the machine direction ($S_{MD}/S_{CD} < 1$), and this pattern holds true for filled papers as well (see Table 5).
The introduction of zeolite fillers leads to a decrease in stretching in both directions; this effect is most pronounced for a paper sample with a high copper content P-CuHCR. In most paper samples, the stretch in the cross direction decreases to the greatest extent, but for the silver-containing paper sample P-AgHCR, the stretch in the machine direction changes more strongly, and in the zinc-containing paper sample P-ZnHCR, the stretch in the cross direction practically does not change (Table 5).

Accelerated aging of ordinary paper P leads to a decrease in stretching mainly in the machine direction. If we compare stretching in aged filled paper with the indicators of ordinary paper (see columns 4 and 5 of Table 6), then in most paper samples the percentage elongation decreases, this effect is most pronounced for a paper sample with a mixture of fillers P-(½Cu+½Zn)HCR. In a number of samples
(P-ZnHCR\textsubscript{1} and P-(\frac{1}{2}Cu+\frac{1}{2}Zn)HCR), the elongation changes more strongly in the machine direction, in other samples (P-HCR, P-CuHCR\textsubscript{2}, P-ZnHCR\textsubscript{2} and P-(\frac{3}{4}Zn+\frac{1}{4}Cu)HCR), the elongation changes more strongly in the cross direction; of particular interest is a sample of paper with a high copper content P-CuHCR\textsubscript{2}, in which \(S\text{MD}/S\text{CD}>1\). In the silver-containing sample of P-AgHCR paper the percentage elongation increases in both directions, in copper containing sample of P-CuHCR\textsubscript{1} paper the percentage elongation increases in the cross direction and decreases slightly in the machine direction.

If we compare the stretching in aged filled paper with the indicators of aged ordinary paper (see columns 6 and 7 of Table 6), then in most paper samples the percentage elongation increases, this effect is most pronounced for the silver-containing paper sample; a significant reduction in elongation is observed only for a paper sample with a mixture of fillers P-(\frac{1}{2}Cu+\frac{1}{2}Zn)HCR.

**Conclusions**

The tensile strength of paper filled with metal-containing bactericidal zeolites depends on the nature of the filler and its metal content.

The introduction of pure zeolite filler HCR and most of the metal-containing fillers into the structure of the paper evenly reduces the strength of the binding of the fibers in both directions, however, the introduction of the silver filler AgHCR and, in particular, the filler with a low copper content CuHCR\textsubscript{1} leads to an increase in the tensile strength in both directions, which indicates the promotion of these fillers enhance the bonding between the paper fibers. Accelerated aging of most papers leads to a decrease in tensile strength mainly in the machine direction, but Ag and Cu+Zn papers show the opposite effect.

The percentage elongation in the cross direction is greater than in the machine direction, and for filled paper, it is also strongly dependent on the nature and metal content of the filler. This indicates the impact of metal-containing zeolites on the binding forces between paper fibers, and the influence of the nature and content of metals in the filler changing indices of elongation is enhanced in aged paper, making some of them more resistant to aging.

It should be noted that the mechanism of the effect of metal-containing zeolites
on the binding forces between paper fibers is unclear and requires further study.

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References:

1. Crowley, R.P. (1966). Method of preparing adsorbent filter paper containing crystalline zeolite particles, and paper thereof. United States Patent Office, 3,266,973 A. https://patents.google.com/patent/US3266973A/en
2. Narayanan, S., Batchelor, W., Webley, P.A. (2013). A review on the use of zeolites to create valuable paper products and paper-like adsorbent materials. Appita: Technology, Innovation, Manufacturing, Environment, 66(3), 235-245. https://search.informit.org/doi/10.3316/informit.426324938402492
3. Zhang Quanchang, Su Mingdi, Dai Changlu, Yang Huarui, Zhang Qixing, Zhang Zhiguo. (1985). Use of clinoptilolite in paper industry as filler of paper. Studies in Surface Science and Catalysis (Editors: B. Držaj, S. Hočevar, S. Pejovnik), 24, 531-538. https://doi.org/10.1016/S0167-2991(08)65322-7
4. Class, C.P., Sikora, M.D. (2007). High performance natural zeolite microparticle retention aid for papermaking. United States Patent, US 7.201.826 B2. https://patents.google.com/patent/US7201826B2/en
5. Ban, W., Thomas, G.S. (2015). Methods to control organic contaminants in fibers using zeolites. World Intellectual Property Organization, WO 2015/026507 A1. https://patents.google.com/patent/WO2015026507A1/en
6. Niira, R., Yamamato, T., Ushida, M.D.-K. (1988). Antibiotic zeolite. European Patent Office, 0 270 129 A2. https://patentimages.storage.googleapis.com/11/4d/6e/6ba315707d3e27/EP0270129B1.pdf
7. Tsitsishvili, V., Dolaberidze, N., Mirdzveli, N., Nijaradze, M., Amiridze, Z. (2021).
Preparation of bactericidal fillers from Georgian heulandite-clinoptilolite and their application for paper production. I. Bactericidal fillers. *InterConf*, 67, 340-358. https://doi.org/10.51582/interconf.19-20.07.2021.037

8. Vergara-Figueroa, J., Alejandro-Martín, S., Pesenti, H., Cerda, F., Fernández-Pérez, A., Gacitúa, W. (2019). Obtaining nanoparticles of Chilean natural zeolite and its ion exchange with copper salt (Cu²⁺) for antibacterial applications. *Materials*, 12(13), 2202-2220. https://doi.org/10.3390/ma12132202

9. Rieger, K.A., Cho, H.J., Yeung, H.F., Fan, W., Schiffman, J.D. (2016). Antimicrobial activity of silver ions released from zeolites immobilized on cellulose nanofiber mats. *ACS Appl. Mater. Interfaces*, 8(5), 3032-3040. https://doi.org/10.1021/acsami.5b10130

10. Lin, Y., Xueren, Q. (2019). Functionally modified zeolite powders for delivering antibacterial performance to cellulosic paper. *Key Eng. Mater.*, 807, 141-150. https://doi.org/10.4028/www.scientific.net/KEM.807.141

11. Tsitsishvili, V., Dolaberidze, N., Mirdzveli, N., Nijaradze, M., Amiridze, Z. (2021). Preparation of bactericidal fillers from Georgian heulandite-clinoptilolite and their application for paper production. II. Bactericidal paper. *InterConf*, 67, 359-374. https://doi.org/10.51582/interconf.19-20.07.2021.038

12. Demirci, S., Ustaoğlu, Z., Yılmazer, G.A., Sahin, F., Baç, N. (2014). Antimicrobial properties of zeolite-X and zeolite-A ion-exchanged with silver, copper, and zinc against a broad range of microorganisms. *Appl. Biochem. Biotechnol.*, 172(3), 1652-1662. https://doi.org/10.1007/s12010-013-0647-7

13. Tsitsishvili, V., Dolaberidze, N., Mirdzveli, N., Nijaradze, M., Amiridze, Z. (2019). Bactericidal adsorbents obtained by ion exchange modification of natural phillipsites. *Chemistry, Physics and Technology of Surface*, 10(4), 327-339. http://dx.doi.org/10.15407/hftp10.04.327

14. Tsitsishvili, V., Dolaberidze, N., Mirdzveli, N., Nijaradze, M., Amiridze, Z. (2020). Properties of bactericidal adsorbents prepared from Georgian natural analcime and phillipsite. *Bull. Georgian Natl. Acad. Sci.*, 14(4), 25-33. http://science.org.ge/bnas/t14-n4/04_Tsitsishvili_Physical-Chemistry.pdf

15. Rusch, R.H. (1931). Accelerated aging test for paper. *Bureau of Standards Journal of Research*, 7, 465-475. https://doi.org/10.6028/JRES.007.026 ; https://nvlpubs.nist.gov/nistpubs/jres/7jresv7n3p465_A2b.pdf

16. Technical Association of the Pulp and Paper Industry (1998). Tensile properties of paper and paperboard (using constant rate of elongation apparatus. *Tappi*, T499-om06. https://www.tappi.org/content/sarg/t494.pdf; http://grayhall.co.uk/BeloitResearch/tappi/t494.pdf