MILUN M. KRGOVIĆ[1]
NADA Z. BLAGOJEVIĆ[1]
NIKOLA BLAGOJEVIĆ[2]

[1]Faculty of Metallurgy and Technology, University of Montenegro, Podgorica
[2]Faculty of Technology and Metallurgy, Beograd

SCIENTIFIC PAPER

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COMPARATIVE POSSIBILITIES OF USING LIMESTONE "VISOČICA" AND DOLOMITE "VIRPAZAR" AS FILLERS IN PAPER PRODUCTION

Non–metallic mineral fillers strongly influence the characteristics and quality of paper. "Visočica" limestone and "Virpazar" dolomite were used to prepare paper samples in this study. The characteristics of such paper samples produced on a laboratory paper machine are presented. The used fillers and paper pulp were also characterised. The following paper characteristics were investigated: gramature, thickness, softness, air permeability, resistance to tearing and stretching, paper ash and retention. The experiments were performed in order to compare the influence of the physico–chemical and structural qualities of the examined carbonate type fillers on the paper properties. The results of the investigation indicated the technological reasons for using these non–metallic mineral raw materials as fillers in the paper industry regarding the mechanical paper characteristics, as well as other properties.

Various additives, which also influence paper quality are used in paper production, besides the basic raw materials i.e. cellulose fibres [1]. Some types of paper (SC – papers, offset, deep–printing papers), beside the basic raw materials (cellulose fibres), use different adhesives, pigments and also a high percentage of fillers, even up to 25 wt.% [2,3]. Non–metallic mineral fillers, beside their positive characteristics, also have negative effects in paper production, for example, high aggregate abrasion in mass preparation, especially on the wet part of the paper machine, i.e. on the basic part of the installation [4]. For the connection of fillers inside the paper, beside the used retention agents [5], the granulometric and mineral content of fillers also have an important role [6,7].

EXPERIMENTAL

Because of the nature of the experiments, the investigations in this paper were divided into several groups:

– physico–chemical and structural characterisation of the chosen fillers,

– cellulose characterisation,

– paper pulp characterisation and

– the production and characterisation of experimental sheets of paper.

Procedure for the determination of the physico–chemical and structural characteristics of the chosen fillers

The mineral composition of "Visočica" limestone and "Virpazar" dolomite was determined by X–ray diffraction on a PHILIPS PW 1730 generator, which has the following characteristics:

– PW 1050/70,

– Cu radiation (35 KV, 20 mA),

– Monochromator AMR (Advanced Metals Research Corporation).

A 72 000 S X–ray quantometer was used to determine the chemical composition of the non–metallic fillers. Microscopy of the non–metallic filler grains was performed on a JEOL JSM 840 scanning microscope. The whiteness of the fillers was determined according to JUS H.N8.138 standard, on an Opton Elrepho R–46 apparatus, which was standardized relative to MgO 86%. The filler density was determined by the pycnometric method and the particle distribution size was determined by the Andreasen method. Filler abrasion was determined by the Valey method. The results of abrasion were obtained according to the JUS B.B8.088 standard. The humidity was determined by drying to constant mass at 105°C.

Determination of the paper pulp characteristics

Two types of cellulose were used to produce the paper samples:

– deciduous white sulphate cellulose "Matroz", Sremska Mitrovica,

– conifer white sulphate cellulose "Bratsk", Russia.

The relation between deciduous and conifer cellulose was 70 wt.% deciduous to 30 wt.% conifer cellulose. The paper pulp pH value was determined using an Iskra 5724 apparatus with a standard saturated calomel and glass electrode. The apparatus was calibrated with pH=4 and pH=9 buffer solutions. After adding the fillers (10, 20 and 30 wt.%) the cellulose grinding degree was determined on a Scooper Riegler apparatus. The results were expressed in °SR, because of the different structure and quality of deciduous and conifer cellulose. Deciduous cellulose is ground in most cases to 37–38 °SR and conifer cellulose to 40–42 °SR. The dry material content was determined according to the JUS H.N8.135 standard. The dry material content for a randomly chosen gramature (75 g/m^2) was 2.4%.

Adresa autora: M.M. Krgović, Faculty of Metallurgy and Technology, Cetinjski put b.b, University of Montenegro, Podgorica,
E-mail: milun@cg.ac.yu
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Procedure for production and characterisation of paper samples

The paper samples were produced according to the JUS H.N8.160 standard on a Frank apparatus. The production process involved the preparation of cellulose and fillers. Cellulose (70 wt.% of deciduous to 30 wt.% of conifer cellulose) was ground first on a Valley holender. Afterwards Agran (starch – 0.5 wt.%), 1 wt.% Melakley DP–2 (resin), fillers and, finally the retention agens (0.02 wt.% cartaretin 40 CE) were added. The prepared mixture was transferred to a mixer and then to a cylinder for paper sheet shaping. Water was pressed out from the suspension through a copper net and moved to a Blattbildner apparatus for sheet drying.

The gramature was determined according to the JUS H.N8.225 standard, and the resistance to tearing on a Frank apparatus according to the JUS H.N8.214/ISO 1924 standard. The resistance to stretching was determined on the same apparatus and according to the same standard as resistance to tearing, but on a different scale. The resistance to tearing was determined on a Lorentzen & Wetre apparatus according to the JUS H.N8.215 standard, the resistance to sprinkling on a Mulen apparatus according to JUS H.N8.210, the air permeability on a Garley apparatus according to JUS H.N8.120. The humidity was determined by drying the paper samples to constant mass at 105°C according to JUS H.N8.206 while the whiteness was determined according to JUS H.N8.138 on an Opton Elrepho R–46 apparatus. The ash content in the paper was determined according to JUS H.N8.206.

RESULTS AND DISCUSSION

The results of the chemical analysis, presented in Table 1, show a high content of CaO – 55.6 wt.% (CO_3 – 99.28 wt.%) in "Visočica" limestone and the exceptional purity of "Virpazar" dolomite (the values of the purity of dolomite are very close to theoretical values), CaO – 34.16 wt.%, MgO – 18.43 wt.%.

Table 1. Chemical composition of "Visočica" limestone and "Virpazar" dolomite

Fillers	SiO_2 (wt.%)	CaO (wt.%)	TiO_2 (wt.%)	Fe_2O_3 (wt.%)	MgO (wt.%)	L.I. (wt.%) (1000°C)
Limestone	0.05	55.6	0.02	0.02	–	43.0
Dolomite	0.24	34.16	0.024	0.08	18.43	47.06

The results of the X–ray analysis of "Visočica" limestone show only the presence of the calcium component and the analysis of "Virpazar" dolomite only the presence of dolomite mineral (Fig. 1 and 2).

The degree of whiteness in "Visočica" limestone is 88.7% and in "Virpazar" dolomite 85.5% (Fig. 3). It is considered that the degree of whiteness depends on the

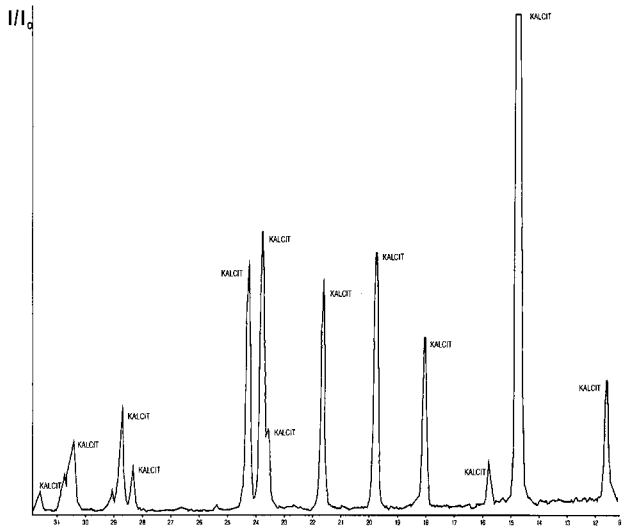

Figure 1. X–Ray diffractogram of "Visočica" limestone

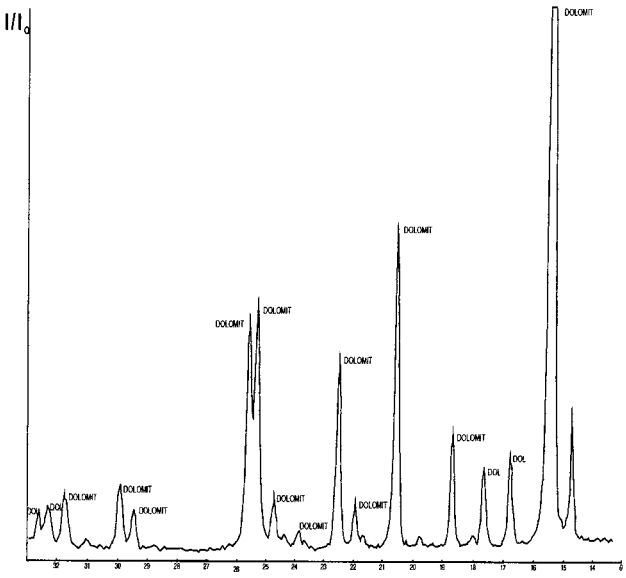

Figure 2. X–ray diffractogram of "Virpazar" dolomite

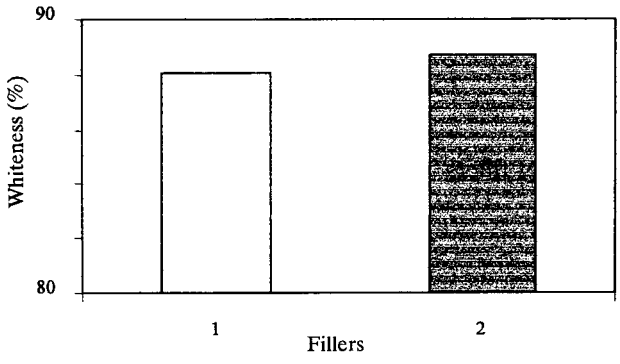

Figure 3. Whiteness of the fillers

Table 2. Physico-chemical characteristics of deciduous cellulose

Characteristics	Value	Standard
Whiteness, Elrepho R-46	89.8%	JUS H.N8.138
pH	7.40	JUS H.N8.124

Table 3. Physico-chemical characteristics of conifer cellulose

Characteristics	Value	Standard
Whiteness, Elrepho R-46	90.20%	JUS H.N8.138
pH	7.50	JUS H.N8.124

Table 4. Paper pulp characteristics

Cellulose species	pH	Grinding degree (°SR)
70 wt.% Deciduous 30 wt.% Conifer	7.3	34

method of preparation of the fillers (the whiteness degree can be increased by wet grinding in a ball mill). However, in this study fillers were ground in a ball mill using the drying process. Both fillers had relatively low abrasion: 1) "Virpazar" dolomite – 9.40 mg and "Visočica" limestone – 20.50 mg.

Depending on reguested type of paper, the relation between deciduous and conifer cellulose can be different. The ratio between deciduous and conifer cellulose was 70 wt.% of deciduous to 30 wt.% of conifer cellulose for the production of experimental sheets of paper. The physico-chemical characteristics of deciduous and conifer cellulose are presented in Tables 2 and 3.

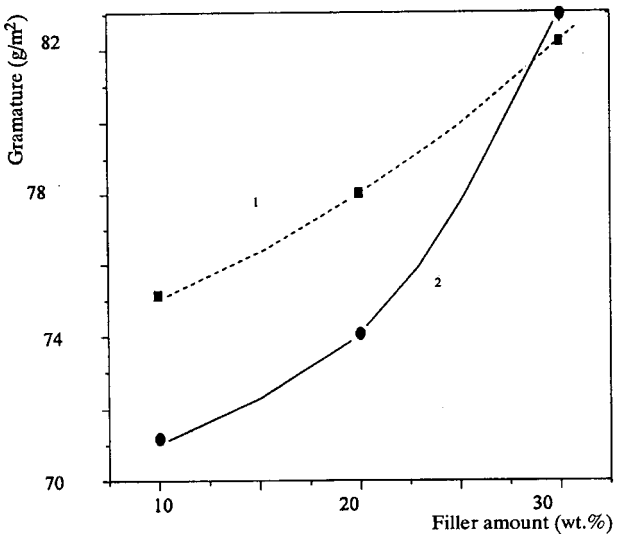

Figure 4. Dependence of the paper gramature on filler type: 1) limestone; 2) dolomite

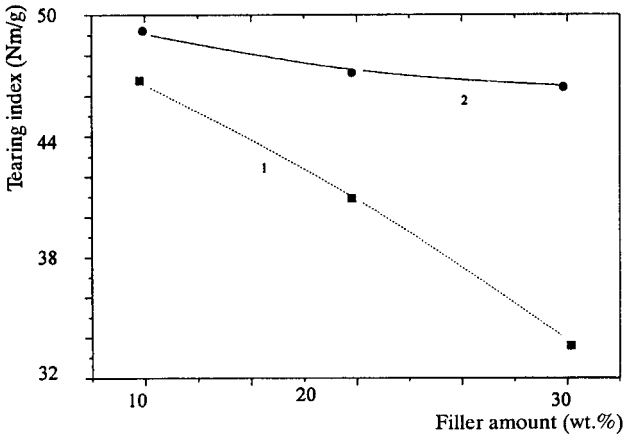

Figure 5. Dependence of the tearing index on filler type: 1) limestone; 2) dolomite

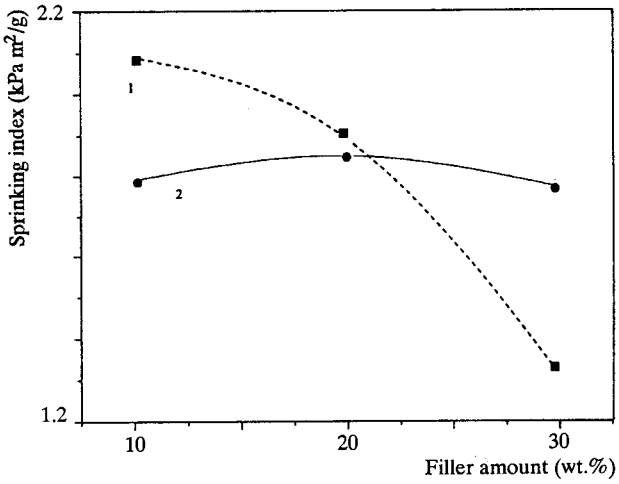

Figure 6. Dependence of the sprinkling index on filler type: 1) limestone; 2) dolomite

In order to reduce the number of variable parameters, the pH and paper pulp grinding degree were kept constant (Table 4).

The values of the paper gramature increase significantly with increasing filler amount (Fig. 4).

Some paper characteristics (softness, permeability, resistance to tearing and stretching, resistance to sprinkling) were demonstrated by using indexes (ratio of the corresponding values and the gramature). The index for tearing and the index for sprinkling decreased with the increasing filler amount (Fig. 5 and 6), which is especially visible in the case of 30 wt.% "Visočica" limestone.

The whiteness of the paper samples is higher in the case "Visočica" limestone is used. With increasing amount of both fillers, the whiteness of the paper samples decreases, which was expected considering the significant whiteness degree in the used cellulose (Fig. 7).

Due to the used retention agent and filler characteristics, the bonding of the fillers is very important which was proved by the ash content in the paper (Fig. 8).

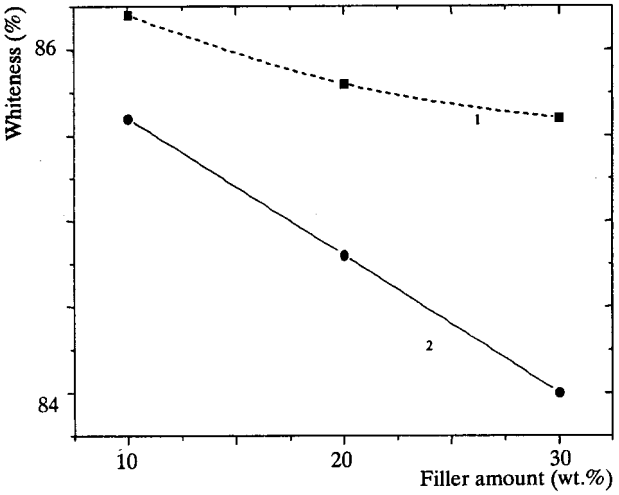

Figure 7. Dependence of the whiteness on filler type: 1) limestone; 2) dolomite

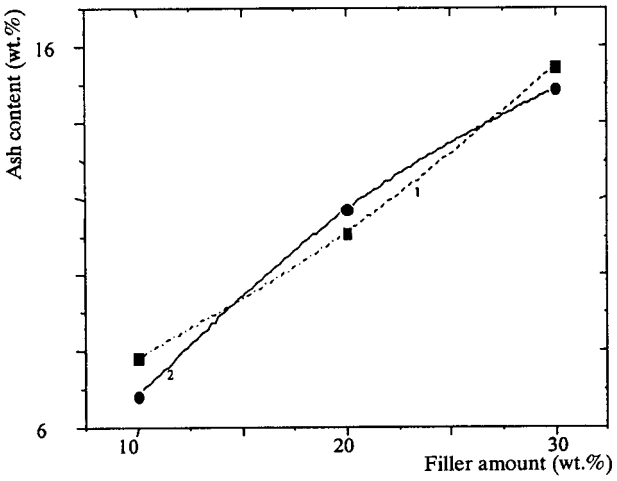

Figure 8. Dependence of the ash content on filler type: 1) limestone; 2) dolomite

However, there are some minimal differences in ash content for these two fiber types.

CONCLUSION

These experimental investigations demonstrate that the usage of "Visočica" limestone and "Virpazar" dolomite as fillers in the paper industry are technologically justified. These two types of fillers are very pure non – metallic mineral raw materials considering their mineral content, they have significant whiteness and relatively low abrasion. Using them as fillers for the production of paper samples on a laboratory paper machine, satisfactory mechanical and other paper characteristics were obtained (resistance to tearing and stretching, air permeability, spalling, whiteness, ash paper, retention). The connection of the fillers in the paper is also very important, thanks to the used retention agent and the filler characteristics, which the results of the ash content and retention demonstrate. A high quality final product might be obtained when these carbonate fillers are used in the paper industry.

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IZVOD

KOMPARATIVNE MOGUĆNOSTI KORIŠĆENJA KREČNJAKA "VISOČICA" I DOLOMITA "VIRPAZAR" KAO PUNILACA U PROIZVODNJI PAPIRA

(Naučni rad)

Milun M. Krgović[1], Nada Z. Blagojević[1], Nikola Blagojević[2]
[1]Metalurško–tehnološki fakultet, Univerzitet u Crnoj Gori, Podgorica
[2]Tehnološko–metalurški fakultet, Univerzitet u Beogradu, Beograd

Ispitana je mogućnost primjene nemetalnih mineralnih punilaca krečnjaka "Visočica" i dolomita "Virpazar" kao punilaca u industriji papira. Određena su fizičko–hemijska i strukturna svojstva punilaca, fizičko–hemijske osobine lišćarske i četinarske celuloze, karakteristike papirne pulpe i izvršena izrada eksperimentalnih listova papira na laboratorijskoj papir mašini za različite unose punilaca (10, 20, 30 mas.%). Postignute su zadovoljavajuće mehaničke i druge karakteristike papira (gramatura, otpornost na kidanje i istezanje, propustljivost, cijepanje, bjelina, pepeo u papiru i retencija).

Ključne riječi: Celuloza • Papir • Papirna pulpa • Punioci • Retenciona sredstva •
Key words: Cellulose • Paper • Paper pulp • Fillers • Retention agens •