

# CELULOZĂ ȘI HÂRTIE

VOL.59

NO. 3/2010

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*Quarterly journal edited by* **THE TECHNICAL ASSOCIATION FOR ROMANIAN PULP AND PAPER INDUSTRY and**

**PULP AND PAPER R&D INSTITUTE – SC CEPROHART SA – Brăila, Romania**

*Sponsored by* **THE ROMANIAN OWNERSHIP OF PULP AND PAPER INDUSTRY**

**ISSN: 1220 - 9848**

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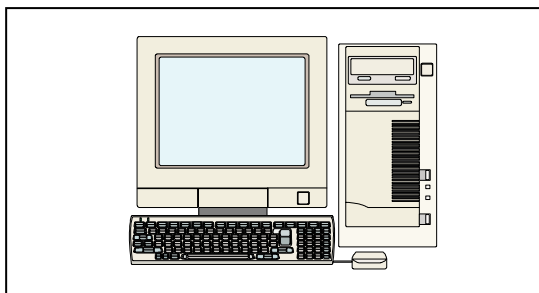
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Aknowledged in Romania, in the Polymer Materials Sciences field, by the National Council of the Scientific Research from the Higher Education (CNCSIS), C group. Indexed in PaperBase Abstracts, PIRA International ([www.paperbase.org](http://www.paperbase.org), [www.piragnet.com](http://www.piragnet.com))

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## IMPACT OF UNUSABLE MATERIAL CONTENT FROM RECOVERED PAPER ON RECYCLING EFFECTIVENESS. CASE STUDY

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### Abstract

Processing of recovered paper determines generation of large quantities of refusals and consumes important quantities of electrical energy. Performance of a recovered paper plant (yield and purity of wanted material) mainly depends on unusable materials content of recovered paper. It is obvious that as the unusable materials content of recovered paper is increasing, the performance of a recovered paper line decreases. As consequence, a better sorting of recovered paper leads to the enhancing the processing of recovered paper and to the lowering the environmental impact. This paper focused on studying the impact of unusable materials content of recovered paper (RP) on waste generation and electrical energy consumption in a recovered paper plant. Trials were performed at industrial scale, in a paper mill producing testliner from recovered paper for corrugated board. Recovered paper having different unusable materials content was processed, and rejects (coarse and fine) were determined. Electrical energy consumption during the recovered paper processing was recorded also. The impact of RP purity on of the waste generation showed that as the unusable materials content increases, the quantities of all kind of rejects are increased. The loss of fiber strongly correlates with unusable materials content of recovered paper. As regarding electrical energy consumption, there is not a clear correlation with unusable materials content in RP. The key parameter influencing waste generation and energy consumption in recycling process is purity of recovered paper grade.

**Key words:** *Recovered Paper, Sorting, Contaminants, Rejects, Energy Consumption*

### Rezumat

La prelucrarea maculaturii se generează cantități mari de refuzuri și se consumă o cantitate importantă de energie electrică. Performanța instalației de prelucrare a maculaturii (cantitatea și puritatea pasteii) depinde de conținutul de materiale neutile din maculatură. Se cunoaște faptul că odată cu creșterea conținutului de materiale neutile din maculatură, performanța instalației se reduce. Prin urmare este de așteptat ca o mai bună sortare a maculaturii să determine îmbunătățirea procesului de prelucrare și să reducă impactul asupra mediului. Lucrarea studiază modul în care conținutul de materiale neutile influențează cantitatea de refuzuri și consumul de energie electrică a unei instalații de prelucrare a maculaturii. Experimentările au fost realizate la scară industrială, într-o fabrică de hârtie care produce testliner din maculatură pentru cartonul ondulat. S-au prelucrat cantități de maculatură cu conținut variabil de contaminanți și s-au determinat cantitățile de refuzuri rezultate. S-a înregistrat și consumul de energie electrică la prelucrarea maculaturii. Studiul influenței purității maculaturii asupra formării refuzurilor arată faptul că odată cu creșterea conținutului de materiale neutile, se mărește și cantitatea de refuzuri generate de instalație. Pierderile de fibră se corelează cu conținutul de impurități din maculatură. În privința consumului de energie electrică, nu s-a observat o dependență clară de conținutul de impurități din maculatură. Indicatorul principal care influențează cantitatea de refuzuri și eficiența instalației de prelucrare este conținutul de contaminanți din maculatură.

**Cuvinte cheie:** *Maculatură, Sortare, Impurități, Refuzuri, Consum de Energie*

## INTRODUCTION

The quality of RP supplied to paper mills impacts the sustainability of paper recycling by influencing the paper recycling chain, but mainly the processes, resources, consumption and emissions in the paper mill. The low quality of recovered paper is due to the high content of unusable components (non-paper and paper and board detrimental to production) which, during recycling, will lead to:

- Low yield of recovered paper processing (recycled fibre flow to paper machine / recovered paper flow in the processing plant), resulting in: direct economic impact, due to the increase of fibre raw material cost per ton of recycled paper; environmental impact, associated with increases in the wet waste volume generated in RP processing, as well as with energy consumption for wet waste management, as a function of the end-of-life solution selected.
- Low quality of recycled pulp, associated with the increase in the short fibres, ash, and stickies content, originated in recovered paper contamination, can produce: economic impact, due higher costs with energy, chemicals or virgin fibres needed to keep the quality of the end product constant; environmental impact, due to the higher energy and water consumption and associated emissions.

RP processing always generates loss of material as rejects. Typical dry basis yields of 90% are obtained with OCC (1.04 and 1.05 grades). Graphic papers (1.11 grade) often have 75-88% yields, although some yields below 70% have been reported, particularly when processing

mainly coated waste paper [1]. The yield loss represents solid wastes and dissolved or very fine material which ends up in the aqueous effluent. Usually 1- 4% of the original RP weight ends up in the aqueous stream, and the rest becomes solid waste [2].

At present, it is recognized that there is not an optimal collection system which can be considered as universal, because it depends on social and economic factors, different at regional and even local level. For this reason, the recovery strategy has to include a sorting process allowing the separation of different components of recovered paper and its classification as EN 643 grades. Sorting is the very first stage, after collection, where the non-paper, paper and board that are non-recyclable or unsuited to the grade have to be removed [3]. Practically, the method and intensity of sorting determine the quality (the type and content of different contaminants) of the recovered paper supplied to the paper mill.

A certain level of contamination of RP always exists, but it has to be minimized as, the lower the quality, the more limited the application of recovered paper as a secondary raw material is. This limitation is due to the fact that the use of recovered paper in paper industry involves a complex process with multiple stages for the treatment of recovered paper, to separate and eliminate the contaminants and finally to obtain the recycled pulp. A global view on recovered paper processing is presented in Figure 1.

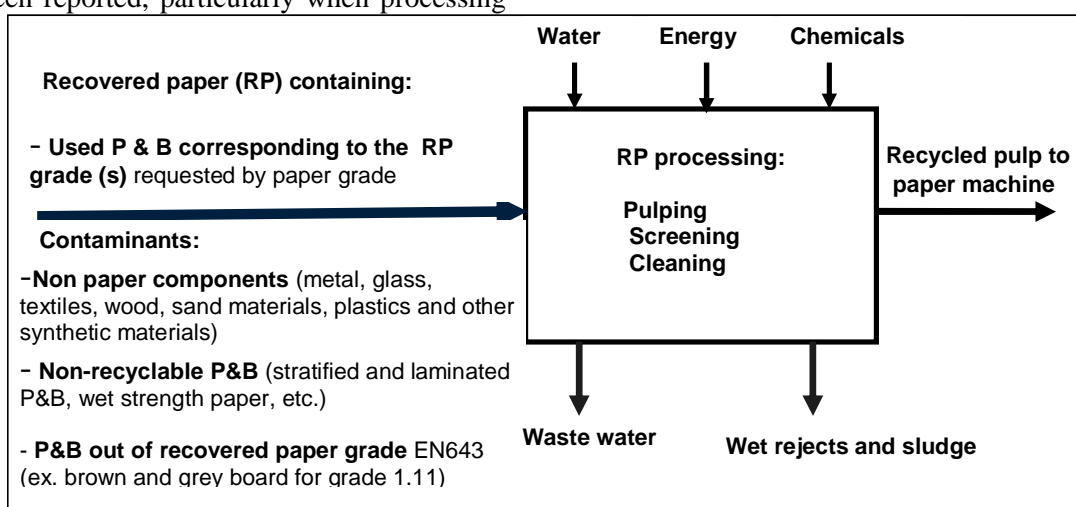


Fig. 1 Inputs and outputs of a recovered paper processing system, [4]

This paper focused on the general objective of the SORT-IT project: to enable sustainable and cost-effective paper recovery at above 95% yield of all recyclable paper and board grades, and to provide recovered qualities of least 98% purity that will allow the best possible re-use in paper & board products.

The interactions between unusable materials content of recovered paper and waste generation and electrical energy consumption in a recovered paper plant are presented in this paper. Trials were performed at industrial scale, in a paper mill producing testliner from recovered paper.

**MILL – SCALE TRIALS**

Mill-scale experiments were performed at VRANCART paper mill, on a paper machine producing testliner for corrugated board. Supermarket RP (1.04 grade) was used. The flow sheet of RP processing is presented in Figures 2 (RP pulping and coarse screening) and Figure 3 (RP fine screening and cleaning), [5].

The level of contamination of RP was varied between 4-10 % by gradually increasing of tetrapack packages percent, as in presented in

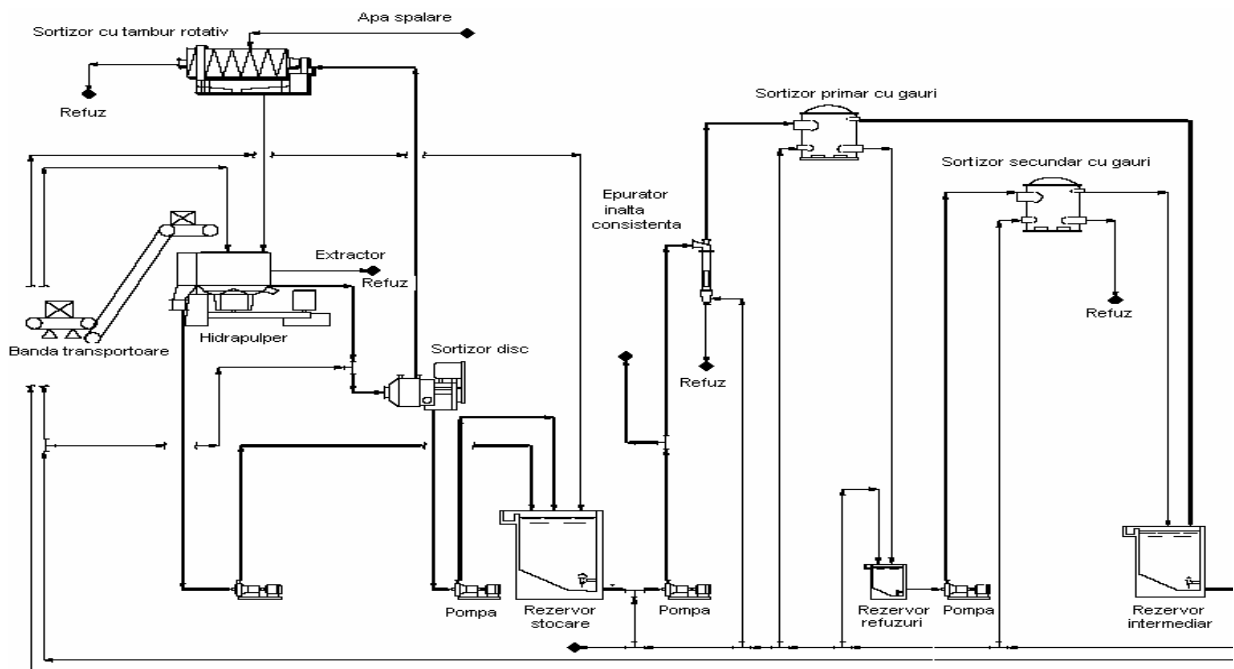
Table 1. The average moisture of RP during the industrial experiments was 10 %.

*Table 1 Composition of RP during the mill trials*

	RP composition	
	RP (1.04), Kg	Tetrapack addition, Kg
4	48.000	0
6	48.000	1870
8	55.000	4160
10	31.000	3530

The mill trials last 3 days, and the running time of paper machine lasts 5-7 hours for every RP quality. The following parameters were evaluated:

- QD – reject generated in secondary pulping stage (o.d);
- PF – fibre content in QD;
- PC – contaminat content in QD;
- QT – reject eliminated by Ragger extractor;
- TF – fibre content in QT;
- TC – contaminat content in QT;
- P – hourly capacity of RP pulping stage
- C – specific power consumption in pulping stage



*Fig. 2 Flow sheet of RP pulping and coarse screening*

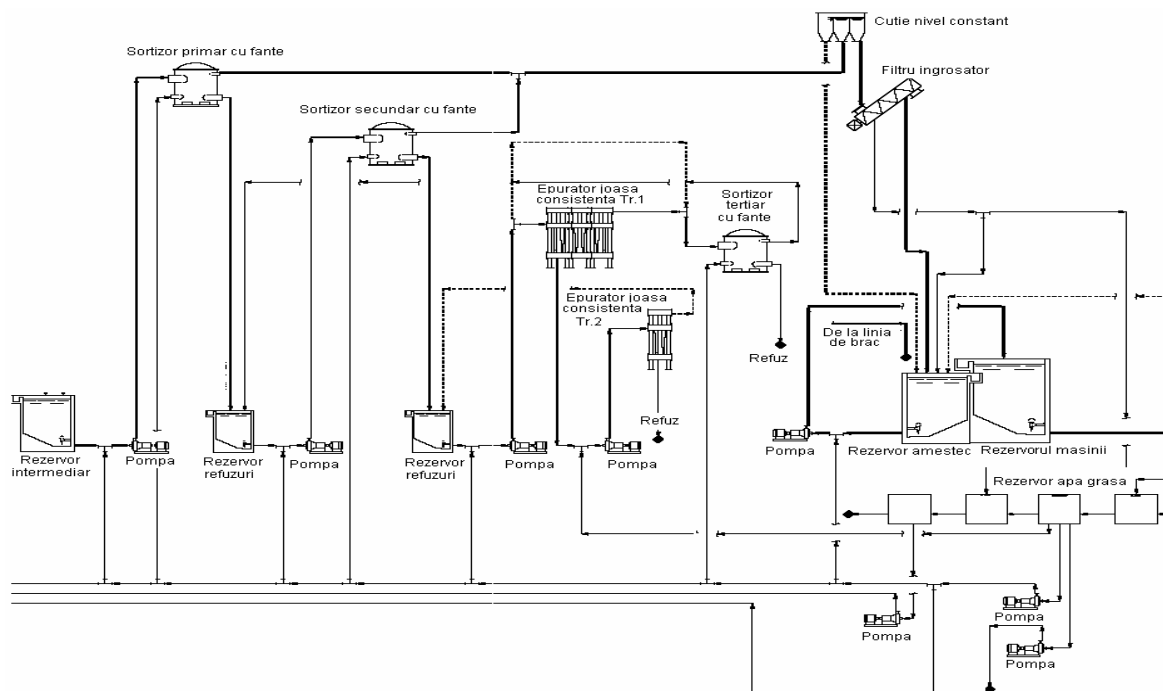


Fig. 3 Flow sheet of RP fine screening and cleaning

## RESULTS AND DISCUSSIONS

The main results of the industrial trials are focused in Table 2.

Table 2 Influence of contamination level on RP processing

Contaminants in RP, (%)	Time of trial, h	RP quantity (t)	P (t/h)	QD (kg/t)	PF (kg/t)	PC (kg/t)	QT (kg/t)	TF (kg/t)	TC (kg/t)	C (kWh/t)
4	10	94	8.94	4.3	1.3	3.05	1.76	0.81	0.95	33.56
6	6	49.9	8.72	7.58	3.03	4.54	2.20	1.12	1.08	34.4
8	7	59.2	8.18	11.6	5.57	6.09	2.64	1.48	1.16	36.67
10	5	34.5	7.55	17.1	9.37	7.80	3.96	2.10	1.86	39.73

Table 2 shows that the increasing of contamination leads to the decreasing of capacity in RP pulping stage. If the level of contamination increases from 4 to 10 %, the productivity of RP pulper decreases by 15.5 % and specific energy consumption increases by 18.4 %. At the same time, an overall increase of rejects and fiber loss takes place. For example, rejects eliminated by Ragger extractor are more than two times higher if RP contamination increases from 4 to 10 %. As regarding fiber loss, when the level of RP contamination increases, the percentage of fiber in rejects increases as well. The evolution of fiber content in QD (table 2) shows a drastic increasing, from 30 % (4% contamination) up to 55 % (10 % contamination).

A more suggestive correlation between RP contamination and pulper capacity and specific power consumption in pulping stage is presented in Figure 4.

As the level of contamination increases, the consumption of electrical energy in pulping stage also increases.

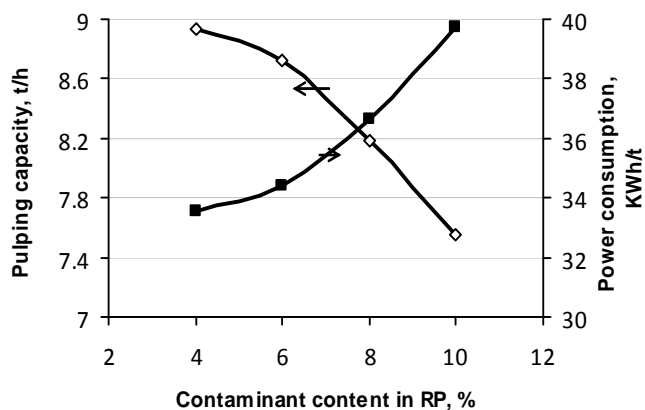


Fig. 4 Influence of RP contamination on pulper capacity and electrical energy consumption in pulping stage

Influence of RP contamination on plant productivity and specific energy consumption is presented in Table 3 and Figure 5. It is obvious that as the contamination increases, the productivity of RP plant decreases and energy consumption increases.

Table 3 Influence of RP contamination on pulp plant productivity and specific energy consumption

Contaminants in RP, (%)	P (t/h)	Screened pulp to paper machine, (t/h)	Specific power consumption of RP plant, (kWh/t)
4	8.94	7.60	112.37
6	8.72	7.23	118.12
8	8.18	6.63	128.80
10	7.55	6.04	141.39

The quantity of recycled pulp supplied to paper machine decreases with 20.5 % and specific energy consumption of RP processing increases with 25.9 %. These figures show the importance of contamination level on performance of a RP processing plant.

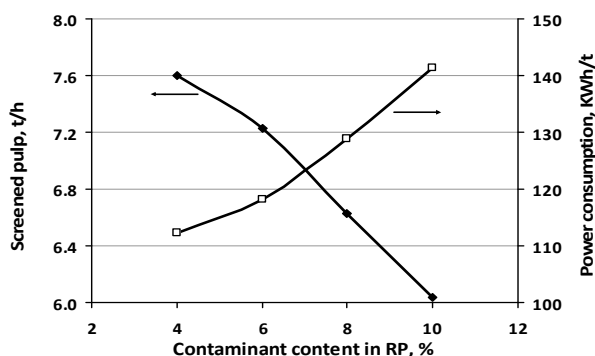


Fig. 5 Dependence between RP contamination and pulp plant productivity and energy consumption

Contamination level is the main parameter influencing specific RP consumption in paper production. Table 4 shows the dependence between contamination level and specific RP consumption in producing testliner grades.

Table 4 Dependence between contamination level and specific RP consumption in producing testliner grades

Contaminants in RP, (%)	RP quantity, (t)	Total rejects, (t)	Total rejects, (%)	Specific RP consumption, (t/t)
4	94	5.751	6.1	1.061
6	49.9	4.879	9.77	1.098
8	59.2	8.473	14.31	1.143
10	34.5	7.286	21.12	1.211

Total rejects rate of the RP plant (includes fiber loss) strongly correlates with contamination level of RP. In order to keep the final pulp cleanliness it is necessary to rise the reject ratio in pulp screening and cleaning stages. By increasing of rejects ratio, specific RP consumption per tone of paper increases, as is presented in Figure 6.

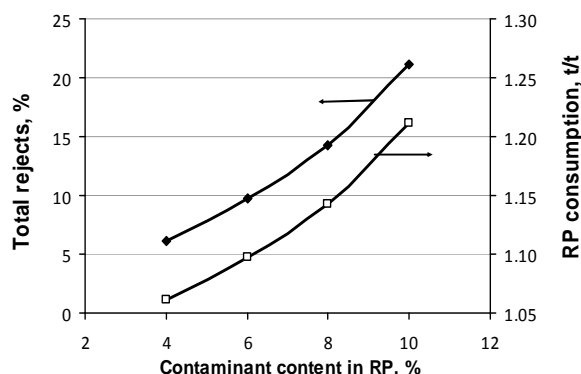


Fig. 6 Influence of contamination level on specific RP consumption in testliner production

Figure 6 shows that pulp dry basis yields of 94-79 % are obtained if contamination of RP increases in 4-10 % range.

## CONCLUSIONS

Impact of recovered paper contamination on effectiveness of recycling process was investigated at industrial level by progressive increase of RP unusable material content from 4 to 10 %. The records on recovered paper and energy consumptions, as well as of solid waste generation lead to following conclusions:

- Increasing of RP contamination leads to decreasing of capacity in pulping stage with 15.5 % and specific energy consumption increased by 18.4 %;
- The content of good fibers in rejects increases drastic as well from 30 % (4% contamination) up to 55 % (10 % contamination);
- The quantity of RP pulp supplied to paper machine decreases with 20.5 % and specific energy consumption of RP processing increases with 25.9 %. Pulp dry basis yields of 94-79 % are obtained if contamination of RP increases in 4-10 % range

### ACKNOWLEDGEMENTS

Financial support from the Seventh Framework Programme: *Recovered Paper SORTing with Innovative Technologies*, (SORT-IT), grant agreement no.: 211888 is gratefully acknowledged.

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## GENERAL ASPECTS CONCERNING SOIL AND UNDERGROUND WATER POLLUTION AT PULP AND PAPER MAKING

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### Abstract

The main problems the present paper is focused on regard the study of investigation and evaluation ways concerning soil and undersoil pollution and recovery of affected areas, according to environmental legislation in force. The first part of the paper presents some legislative and theoretical aspects concerning the analysis of geological and hydrological environment as well as the depollution methods. The second part of the paper shows a case study regarding remediation of soil affected by historical pollution at pulp and paper making. The study sustains the pulp and papermaking in order to solve the environmental pollution problems and especially, those related to soil and underground water pollution, in order to elaborate the technical interpretative documentation required to get the deeds of arrangement.

**Key words:** *Soil, Underground water, Pollution, Depollution methods*

### Rezumat

În această lucrare sunt prezentate metodele de investigare și evaluare a gradului de poluare a solului și subsolului și reconstruirea zonelor afectate în conformitate cu legislația în vigoare privind protecția mediului. În prima parte sunt prezentate câteva aspecte teoretice și legislative cu privire la analiza geologică și hidrologică și la metodele de investigare. În a doua parte se prezintă un studiu de caz privind remedierea solului afectat de poluarea istorică provenită de la fabricarea celulozei și hârtiei. În studiu se prezintă problemele legate de poluarea solului și a apei subterane și modalitățile de elaborare a documentației tehnice de interpretare în scopul rezolvării lor.

**Cuvinte cheie:** *Sol, Apă subterană, Poluare, Metode de depoluare*

## INTRODUCTION

Natural resources of Romania and industrialization policies prior to 1990 encouraged the development of highly polluting activities in the pulp and paper industry (eg.: bisulphite cooking, bleaching with chlorine, fuel storage, organic and inorganic waste disposal etc.). As a result of execution of these activities, soil and subsoil were contaminated local or regional with natural and synthetic organic substances, heavy

metals, hydrocarbons etc., causing over time the appearance and expansion of contaminated sites which currently affects environmental conditions. This raises serious investigations aimed, such as: risk assessment of contaminated sites for human population and ecosystem components; methods of investigation and assessment of contaminated sites; assuming responsibilities in the investigation and assessment of contaminated sites and establish the most appropriate and

effective methods to remedy the affected areas by historical pollution [1].

In this context, our country is taken a series of laws on soil and subsoil protection of which the most important for our problem is the Government Decision no. 1408/19.11.2007 concerning the investigation and assessment of soil and subsoil pollution and the Government Decision no. 1403/19.11.2007 concerning the restoration of the soil, subsoil and terrestrial ecosystems were affected [2], [3].

The aim of investigating and assessing soil and subsoil pollution is the delimitation of the polluted area, clarifying the nature and intensity of pollution identified, the relationship of pollutants with mineral matrix of rocks and geological environment structure, migration routes and transport of pollutants and risk assessment of geological data necessary to compile programs or geological environmental remediation projects. Investigation of geological environment for assessment of contamination is achieved through specific methods soil, geological and/or hydrogeological, geochemical and geophysical.

Remediation methods of contaminated soil must be determined taking into account on the one hand the total effects of contaminated soil on human health, on the source of water, on ecosystems, on buildings and sites important to the community etc., and on the other hand it must be evaluated in detail, so that it can be known benefits of remediation / decontamination and financial effort that can be achieved. For soil decontamination methods using both physicochemical and biotechnological methods [4].

The best known **Physicochemical methods** are: excavation method, injection method "venting", the method of flotation, electrical extraction method, extraction by heating, washing with solvents, washing with water. Usually physicochemical methods consist of the removal of polluted soil, treating it (with one or more methods above) and then putting it back. Physicochemical methods are generally avoided because of achieving generates huge costs due to transport and storage. But the advantage to solve the problem quickly and may be an optimal solution where time takes precedence over decontamination remediation budget.

**Biotechnological methods** are based on using bacteria or plants for soil remediation. Using bacteria for the remediation to treat, recycle and even eliminate unwanted or dangerous elements in the soil, such as hydrocarbons or heavy metals. Using plant or phyto-remediation can be

performed for the total destruction of pollutants, or for their stabilization in soil. Of remediation techniques with the most popular herbs are phyto-stabilization, phyto-extraction fito-degradation, phyto-volatilization.

## EXPERIMENTAL

Case study, subject of this paper, focused on researching and evaluating soil and subsoil pollution at the site of pulp and paper sector in the country, affected by historical pollution as a result of final cessation of the manufacture of bleached sulphite pulp from softwood and final closure of organic and inorganic waste dump. Investigation and assessment study was done by using a combination of research methods including pedological, hydrological and geochemical. Research methodology consisted of:

- Research of existing and specific data on analysed area;
- Work in the field, direct observation, sampling;
- Geochemical Sampling of soil and groundwater samples;

### A. Research of existing and specific data on analysed area

Following tests carried out by researchers from the Institute of Pedology and Agrochemistry Bucharest, the profile of soil to a depth of 100 cm, showed that the geological environment of the industrial site, as a result of anthropogenic activity, shows specific characteristics of alluvial protosols class with sandy to clayey texture.

Following tests carried out on soil profiles, on samples of plants and vegetal material, results that the geological environment of the adjacent industrial objective, as a result of anthropogenic activity, shows specific characteristics of *clayluvisoil class (brown clay type soils, brown luvis soils and albic luvisols), cambisols class (brown type mesobasic), non-developed or cropped soils class (alluvial protosols and erodidsoil type)*.

From the data provided by existing drilling at the site examined, results that the aquifer levels of first category, groundwater, is encountered at depths than 6-8 m, hydrostatic level is at approx. 1-15 m from ground level, depending of limestone formations in the area. Temporal variation of flow is 6-15 l/s conditioned by: the local rainfall regime, oscillations of the surface water level, emissary river, technical losses in the technological process of analyzed objective, or neighborhoods.

On analyzed site the hydrostatic level lies at a depth of 1.95 m. However, recent excavations carried out on site demonstrate that hydrostatic level is even less than 1 m deep. To the information available from geotechnical studies performed on the platform, in terms of migrating groundwater, river receiving the effluent of analyzed objective is a drain for the area whose groundwater flow direction is parallel to the riverbed.

**B. Work in the field, direct observation, sampling**

The **geotechnical trenches** performed on site revealed a geological sequence represented by: *blocks, gravel and sand in interspaces (crystalline nature and sedimentary), above which were made loamy sand, who constitute alteration crust of the earth (clay-type accumulation) with weak to moderate clay content.*

**Soil samples** were taken from two depths, located at 5 cm, respectively, 30-40 cm from soil surface, under the provisions of Order No. 184/97. Collection points for soil samples are presented in table 1.

*Table 1 Collection points for soil samples*

Plane position	Name of adjacent plant
<b>Zone A</b>	<b>Industrial site - Less sensitive use (site inoperable)</b>
Point: <b>E1</b>	Diesel oil deposit area / dismantled area
Point: <b>E2</b>	Sulfur deposit area / dismantled area
Point: <b>E3</b>	Ammonium sulphite plant area / dismantled area
Point: <b>E4</b>	Storage facilities area and chemical preparation / dismantled area
Point: <b>S4</b>	Fuel-oil tanks, south side / dismantled and monitored area
Point: <b>S5</b>	Bleaching agent preparation plant /dismantled and monitored area
Point: <b>S6</b>	Old waste storehouse, east side / dismantled and monitored area
<b>Zone B</b>	<b>Outdoor enclosure - Sensitive Use</b>
Point: <b>S7</b>	Outside the company enclosure, in the SE side

Soil sampling was done taking into account the following criteria: areas that have been used to temporarily store raw materials, auxiliary materials, fuels containing hazardous substances and / or hazardous waste, the distribution of all cardinal directions, near sources of pollution, including sources of air pollution; to be included soils both of less sensitive use category - Zone A, and the sensitive use category - Zone B

**Groundwater samples** were taken from the two existing drilling site:

- F1 drilling (Diesel oil deposit area);
- F3 drilling (drain of treatment plant).

Groundwater are affected by historical pollution and/or current activities, by wastewater emissions falling to the ground and underground, because of possible leaks from sewage systems, accidental spills from plants, deposits of mud and waste on site and also because of transport phenomena of atmospheric emissions of precipitation fell during the year, especially during Steam Boiler operation on diesel oil. Although concrete platforms were approx. 80% of the enclosure, located on the right side of the

receiver, corrosiveness of working environment and the age of platforms have created possible pathways of pollutants in soil and groundwater.

**C. Geochemical Sampling**

**Soil**

Impact assessment of soil pollution in the area affected by historical pollution - was conducted by SC CEPROHART SA Braila - Research and Design Institute of Pulp and Paper Industry. Investigations have resulted in physical and chemical analysis carried out on soil samples taken from two depths required by law, namely: Ord. 184/1997 and Ord. 756/1997.

Nature and degree of soil pollution were based on physical-chemical analysis results of soil samples collected in the study area: the dismantled - demolished installations and outside the company.

Soil pollution indicators have been established under the provisions of Ord MAPPM no. 184/97 Annex A.3.1, depending on area history, the risk of attack on building materials, the utilizations and the risk of polluting the groundwater pH, sulphates, sulphides, chlorides,

phenols, oil products, nitrates, nitrites, copper, nickel, lead.

Soil samples were pretreated in accordance with ISO 11466 / 1999 by separating coarse material, removing plant debris, drying and mixing the sample, and chemical analysis were performed to determine the nature and extent of pollution.

For the determination of heavy metals: Pb, Ni, Cu, standardized method was applied ISO 11047/98 - "Soil quality. Determination of Cu, Pb, Ni in the aqueous extract with aqua regia" and spectrophotometer DR/2800 of the SC CEPROHART S.A Braila environmental laboratory. Spectrophotometer DR/2800 was used to determine indicators: sulphates, sulphides, phenols, nitrates, nitrites, chlorides, ammonia nitrogen.

**Groundwater**

According to standardized methods have been carried out for the following indicators: pH, COD, ammonium, nitrites, nitrates, sulphides, sulphates, phenols, extractible substances in petroleum ether (ESPE), Cu, Ni, Pb. Heavy metal group analyzed only lead is classified as potentially toxic chemicals, other Ni, Cu, are undesirable chemicals group, elements belonging to the natural composition of water and can cause changes in physical and organoleptic properties of water , making it unfit for consumption. To determine indicators of water pollution, using the DR 2800 spectrophotometer, COD reactor, Multimeter Multi 340i WTH (dissolved oxygen, conductivity, pH) and standard analytical methods.

**RESULTS AND DISCUSSION**

The test results of soil samples are presented in Table 2.

Analysis of data contained in the table it was found that soil samples at both depths, revealed

the presence in soil of all compounds proposed to investigate, as follows:

- pH of soil samples is included in the area: slightly alkaline soil with 7.6 to 7.9 in the sensitive land use - sample S7 and weak acid and neutral soils with values ranging from 5.94 to 7.01 to use less sensitive area;
- Sulphide concentrations at all points analyzed are below the alert threshold;
- Sulphate concentrations in the sensitive area of service below the alert threshold. For industrial use zone points E2, E3 and E4 levels are between warning threshold and the threshold of intervention, but values closer than the action alert threshold;
- Phenol concentrations in the samples from the site at both depths studied below the alert threshold for the type of service covered less sensitive, for use of sensitive values are below normal;
- With regard to petroleum products to points E1 and S4 values are below the alert threshold for the use of less sensitive;
- In all samples from the site at both depths studied, concentrations in metal ions: copper, nickel, lead levels are above normal but lower concentrations to alert thresholds for less sensitive soil.
- The soil blank sample, S7, in the neighborhood of the site, at both depths studied, concentrations of chemical elements in soil are covered under the alert threshold for the type of usage sensitive, although metal concentrations are above the normal usage of sensitive soils.

Table 2 Test results concerning the content of pollutants in soil

[mg/kg dry]

Sample	H, cm	pH	Sulphide	Sulphate	NH4	NO3	NO2	Phenol	Cl	p.p	Pb	Cu	Ni
<b>Zone A Less sensitive land use, industrial use area</b>													
E1	5	6,39	12,5	453	-	-	-	0,14	-	379	68,5	92,1	59,5
	30	6,45	abs	1.235	-	-	-	0,17	-	294	63,6	88,4	70,2
E2	5	6,79	284	11.873	-	-	-	0,38	-	-	76,3	68,9	88,1
	30	6,83	173	10.373	-	-	-	0,33	-	-	79,6	72,6	74,2
E3	5	6,10	163	10.876	13,8	24,7	8,3	0,30	21,4	-	83,0	59,6	99,3
	30	6,32	89	10.173	11,3	19,8	7,6	0,22	19,5	-	73,8	67,2	89,0
E4	5	5,94	29,8	7.451	9,2	10,5	25,3	0,30	14,0	-	109	75,7	74,6
	30	6,02	48,9	6.956	6,7	12,4	19,3	0,33	15,1	-	68,9	69,3	59,2
S4	5	6,91	abs	352	-	-	-	0,21	-	187	65,2	49,6	66,5
	30	7,01	18,5	401	-	-	-	0,24	-	212	70,1	57,9	61,4

Table 2 (continuation)

S5	5	6,21	19,5	1.231	-	-	-	0,15	-	-	49,7	69,1	79,4
	30	6,43	36,3	1.036	-	-	-	0,15	-	-	57,9	74,7	80,8
S6	5	6,83	abs	893	-	-	-	2,30	-	-	85,3	103,	110
	30	6,61	16,8	1.410	-	-	-	3,45	-	-	79,4	129	90,4
<b>Zone B Sensitive land use, agricultural use area</b>													
S7	5	7,82	abs	1.589	-	-	-	0,15	-	-	46,1	75,1	56,7
	30	7,69	11,9	1.682	-	-	-	0,19	-	-	36,2	87,4	45,3
<b>Normal value in soil</b>	-	-	-	-	-	-	-	<0,02	-	<100	20	20	20
<b>Alert threshold sensitive use</b>	-	200	2.000	-	-	-	-	5	-	200	50	100	75
<b>Alert threshold less sensitive use</b>	-	400	5.000	-	-	-	-	10	-	1000	250	250	200
<b>Intervention threshold less sensitive use</b>	-	2.000	50.000	-	-	-	-	40	-	2000	1000	500	500

### Groundwater

Analysis results of groundwater sample are presented in Table 3.

Comparative analysis of values determined for groundwater pollution indicators with Law. 458/2002 amended and supplemented by Law 311/2004 lead to the following issues:

- pH value falls within acceptable limits for all samples;
- There is classification according to regulatory for indicators: ammonium, nitrites, nitrates, sulphates;
- Sulphides are a specific pollutant from pulp and paper industry. Threshold for intervention

is found exceeded to sample groundwater from drilling Diesel oil deposit area F1;

- It highlights the presence in groundwater at very low concentrations of phenols and extractable substances (ESPE)
- COD indicator value, for F1 and F3 is found exceeded, reflecting the share of anthropogenic influence, extensive industrial activity;
- With regard to heavy metal values for Pb and Ni indicators in both wells, exceeding the thresholds for intervention

Table 3 Indicators of groundwater samples

Area location	Sampling place	Data	pH	COD mg O <sub>2</sub> /l	NH <sub>4</sub> <sup>+</sup> mg/l	NO <sub>3</sub> <sup>-</sup> mg/l	NO <sub>2</sub> <sup>-</sup> mg/l	S <sup>2-</sup> mg/l	Sulphates mg/l	Phenol mg/l	Extractables mg/l	Cu mg/l	Ni mg/l	Pb mg/l
Diesel oil storage	F1	2008	7,7	43	-	2,5	-	-	-	0,02	-	-	-	-
		2009	6,71	35	-	0,5	-	-	-	0,00	-	-	-	-
		*2009	6,57	20	0,11	1,0	SLD	0,165	6	0,013	0,57	0,07	0,11	0,14
Drain of Treatment plant	F3	2008	6,96	70	-	2,6	-	-	-	0,095	-	-	-	-
		2009	6,83	14	-	1,4	-	-	-	0,011	-	-	-	-
		*2009	6,84	45	0,23	1,2	0,4	0,006	66	0,012	0,62	0,048	0,172	0,042
Law 458/2002 amended and supplemented by Law 311/2004			6,5-9,5	5	0,5	50	0,5	0,1	250	-	-	0,1	0,02	0,01
Ord.161/ 2006		Class I	6,5-8,5	10	0,4	1	0,01	-	60	0,001	-	0,020	0,010	0,005

### CONCLUSIONS

1. According the analysis performed, geological environment of the adjacent area industrial objective, as a result of anthropogenic activity, presents the following characteristics: **Clayluvisoil Class** (brown clay type soils,

2. brown luvic soils and albic luvisols) **Cambisols class** (brown type mesobasic); **Non-developed or cropped soils class** (alluvial protosoils and erodidsoil type).
2. Since the foundation of the site at depths of more than 1.95 m is composed of porous rocks (gravel, blocks and sand), rainwater

infiltrates into the depths and dissipate historical pollutants.

3. Current and past activities on the site examined lead to an impact on groundwater, by the pollution with oxidisable organic substances, phenols, extractable substances and heavy metals as a cumulative effect of prolonged operation of the pulp and paper mill.
4. However, considering that in many "hot points", the pollution was stopped by the closure of production capacity (eg. Pulp mill), and continue to appreciate gradually decrease the pollution of soil and underground site.
5. In the area of old waste storehouse it is recommended to rebuild the plant surface soil layer at the end of the operation of decontamination, according to the final destination of the land as "sensitive use". Typically, this reconstruction is achieved through well-established farming methods (early rehabilitation overburden layer plant decontamination operation, whether to add the contribution of fertile surface layer in other areas, with appropriate addition of fertilizer - preferably of natural origin, ploughing/disking

soil and seeding of grass species (eg., *Trifolium repens* variety S100, 2.75 kg / ha)

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## EVALUAREA RESURSEI POTENȚIALE DE MATERII PRIME/MATERIALE SECUNDARE A SECTORULUI PAPETAR DIN ROMÂNIA ȘI ANALIZA CONTEXTULUI LEGISLATIV

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### Rezumat

În ultimii ani, industria românească de hârtii și cartoane a evoluat spre producerea de sortimente papetare, care utilizează ca materie primă fibroasă maculatura într-o proporție majoritară, la unele sortimente cum ar fi hârtiile igienico – sanitar și hârtiile de ambalaj și chiar de 100% la hârtiile pentru carton ondulat și hârtia de ziar.

La nivelul anului 2009 cantitatea de maculatură colectată/reciclată s-a cifrat la 324 t, la o rată de colectare de cca. 41% și o rată de utilizare de 93,4%.

În prezent, unitățile de reciclare a maculaturii se confruntă cu o serie de dificultăți privind asigurarea necesarului de maculatură, datorită competiției externe, din ce în ce mai acerbe.

Prezenta lucrare a fost elaborată în perioada 2008-2010 în cadrul Programului Sectorial în domeniul cercetării – dezvoltării în industrie/2008, având drept obiectiv general, creșterea gradului de reciclare, respectiv valorificare a deșeurilor de hârtii și cartoane.

Conform Planului de realizare a proiectului, lucrarea a fost elaborată și structurată pe trei direcții principale și anume:

- Situația actuală și de perspectivă privind necesarul și modul de asigurare cu maculatură al sectorului papetar, comparativ cu țările UE;
- Analiza legislației naționale și europene privind deșeurile, deșeurile reciclabile și deșeurile de ambalaje, precum și implicațiile transpunerii noii Directive cadru privind deșeurile, asupra reciclării interne a maculaturii;
- Propuneri de măsuri/acțiuni pentru creșterea gradului de colectare, respectiv de reciclare a maculaturii, inclusiv prin crearea de operatori zonali de intermediere și centre de colectare a maculaturii proprii sectorului papetar.

**Cuvinte cheie:** *Reciclare, Valorificare, Colectare, Hârtii și Cartoane Recuperate*

### Abstract

The Romanian paper and board industry has developed to the production of paper grades, that use as raw material, a major percentage of recovered paper for sanitary papers and even 100% for container board and newspaper.

In 2009, the collected/recycled recovered paper quantity represented 324 t, at a collection rate of around 41% and a use rate of 93.4%.

At present, the recovered paper recycling units are facing difficulties concerning the provision of recovered paper requirement due to the increasingly keen foreign competition.

The present paper was carried out in 2008-2010 within the Sectoral Research-Development Program in industry/ 2008, having as general objective, the rise of recycling degree, recovery of paper and board waste, respectively.

According to the Project Plan, the paper has been elaborated and structured on three main directions, namely:

- The current and far-reaching situation concerning requirement and way of covering the recovered paper requirement of the paper industry, compared to the EU countries;

- Analysis of the national and European legislation regarding waste, recyclable waste and packaging waste, as well as the implications of transferring the new Waste Framework Directive onto domestic waste paper recycling;
- Proposals of measures/actions to rise the collection rate, the recovered paper recycling rate respectively, including by means of creating intermediation area operators and collection centers of waste paper from the paper sector.

**Key words:** *Recycling, Valorization, Collection, Paper and Boards Recovered*

## INTRODUCERE

### I. Analiza situației actuale și de perspectivă privind necesarul și modul de asigurare cu maculatură a sectorului papetar, comparativ cu țările UE

În cadrul sectorului papetar, care reprezintă singurul valorificator/reciclator pentru maculatură la nivel național, se manifestă în mod ciclic următoarele fenomene specifice economiei de piață:

- Fluctuații mari în oferta de preț și cantitate a colectoarelor;
- Apariția de stocuri mari de maculatură fie la colectori, fie la reciclatori, sau
- Criză de maculatură și prețuri foarte mari;
- Creșterea cererii/ofertei la export și reducerea corespunzătoare a ofertei pentru reciclatorii interni.

În prezent, unitățile de reciclare a maculaturii se confruntă cu mari dificultăți privind asigurarea necesarului de maculatură, datorită competiției externe, din ce în ce mai acerbe.

Astfel că, situația actuală poate fi caracterizată prin:

- Cantitate insuficientă de maculatură pe piață, datorită creșterii dramatice a exportului (cca 5.000 t/lună);
- Creștere continuă a prețurilor (cca 105 – 120 Euro/t în cazul maculaturii din C.O.);
- Înrautățirea calității maculaturii pentru consumul intern, ca urmare a valorificării la export a maculaturii de calitate mai bună;

- Condiționarea livrării maculaturii din c.o. cu livrarea unor cantități de maculatură din ziare și reviste (ca efect al închiderii fabricii LETEA, Bacău).

Principala competiție la care trebuie să facă față la ora actuală reciclatorii din sector este competiția cu exportul.

Exportul de maculatură în anul 2009 a crescut alarmant datorită în principal:

- unor prețuri mai mari și a unor condiții de plată mai avantajoase, oferite colectoarelor de maculatură în cazul exportului,
- apariției unei capacități noi de producție pentru hârtiile miez-capac, mare consumatoare de maculatură, cum este cazul firmei DUNAPACK în Ungaria.

Escaladarea prețurilor la maculatura din România poate pune în pericol asigurarea cu materia primă fibroasă principală a sectorului de celuloză și hârtie, mai ales că în viitorul apropiat, vor apărea pe piață și alți noi consumatori de maculatură din carton ondulat.

*Cum s-a ajuns aici?*

Evoluția principalilor indicatori ai sectorului papetar din România în perioada 2001 – 2009 se prezintă în tabelul 1 și în figurile 1 și 2.



Tabelul 1 Evoluția principalilor indicatori ai sectorului papetar din România

- mii t -

Specificație	2003	2004	2005	2006	2007	2008	2009
Producția de hârtii și cartoane	444	454	371	390	450	360	288
Consumul de hârtii și cartoane	632	677	750	832	964	857	791
Consum intern aparent de maculatură	222	253	248	263	302	330	270
Export de maculatură	8	4	5	12	14	9	58
Import de maculatură	20	9	8	6	7	7	4
Maculatura colectată	210	248	245	269	309	332	324
Rata de colectare/reciclare %	33,2	36,6	32,6	32,3	32,0	38,7	41,0
Rata de utilizare, %	50,0	55,7	66,8	67,4	67,1	91,6	93,4

Sursa: CEPROHART Brăila, ROMPAP și Institutul Național de Statistică

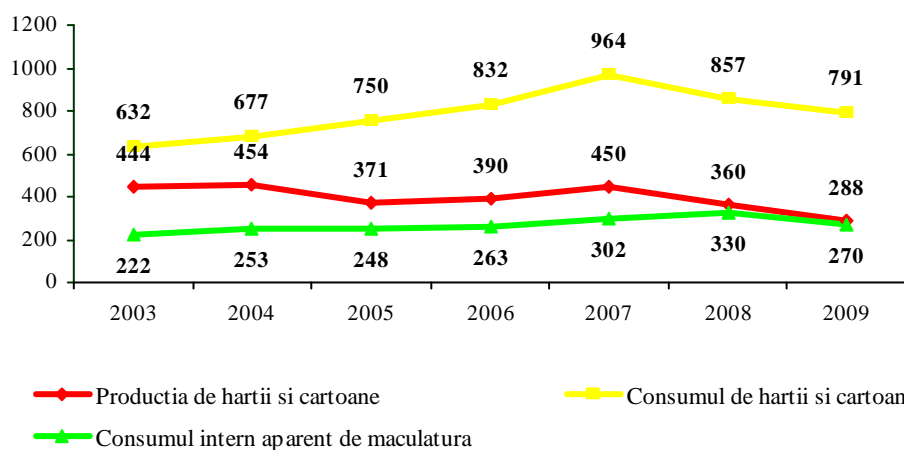


Fig.1 Principalii indicatori economici ai sectorului în perioada 2003-2009

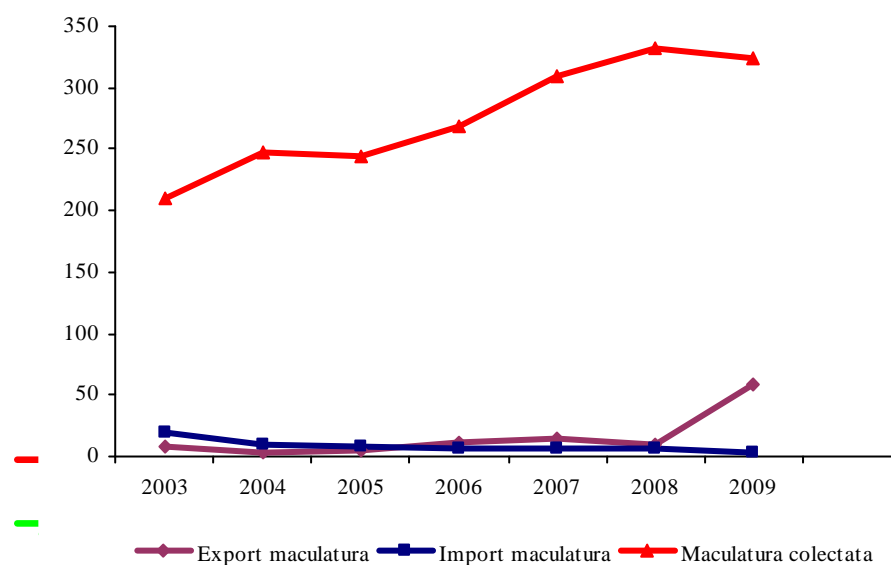


Fig.2 Evoluția exportului, importului și a cantității de maculatură colectată în perioada 2003-2009

Din datele prezentate în tabelul 1, figurile 1 și 2, rezultă că:

- Producția de hârtii și cartoane a cunoscut două vârfuri, în anii 2004 și 2007, când nivelurile de producție au fost de 454 mii tone, respectiv de 450 mii tone, în concordanță cu evoluția economiei din România;
- Începând cu anul 2008 se constată o reducere semnificativă a nivelului de producție, reducerea accentuându-se și mai mult în anul 2009, datorită încetării activității la societățile CELHART DONARIS Brăila, CELROM Tr. Severin, CAHIRO Scăieni și MUCART Cluj, concomitent cu reducerea producției la celelalte societăți;

- Ca urmare a închiderii fabricilor producătoare de celuloză și semiceluloză, industria de celuloză și hârtie din țara noastră a evoluat spre producția de sortimente papetare, care pot utiliza maculatura ca materie primă fibroasă, într-o proporție majoritară, respectiv hârtii pentru carton ondulat, hârtie de ziar și hârtii igienico-sanitare;
- Cantitatea de maculatură colectată în anul 2009 a fost apropiată de cea colectată în anul 2008 (cca 332/324 t), dar rata de colectare a crescut de la 38,7 % la 41 % ; această valoare de 41 % a ratei de colectare se situează însă mult sub cea realizată de media țărilor CEPI de 72,2%;

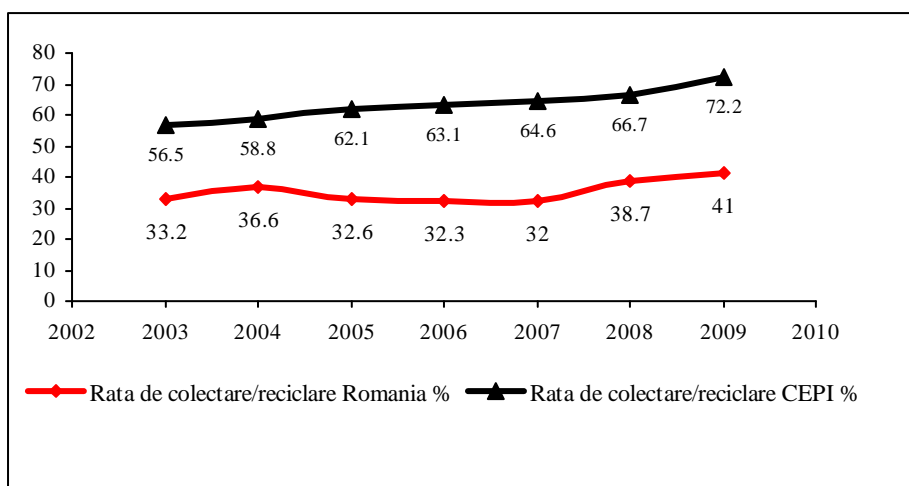


Fig. 3 Evoluția ratei de colectare/reciclare a maculaturii în general, comparativ cu rata de colectare/reciclare CEPI, în perioada 2003-2009

- Rata de utilizare a maculaturii cunoaște un salt semnificativ de la 67,1% în 2007, la 91,6% în 2008 și respectiv 93,4% în 2009;

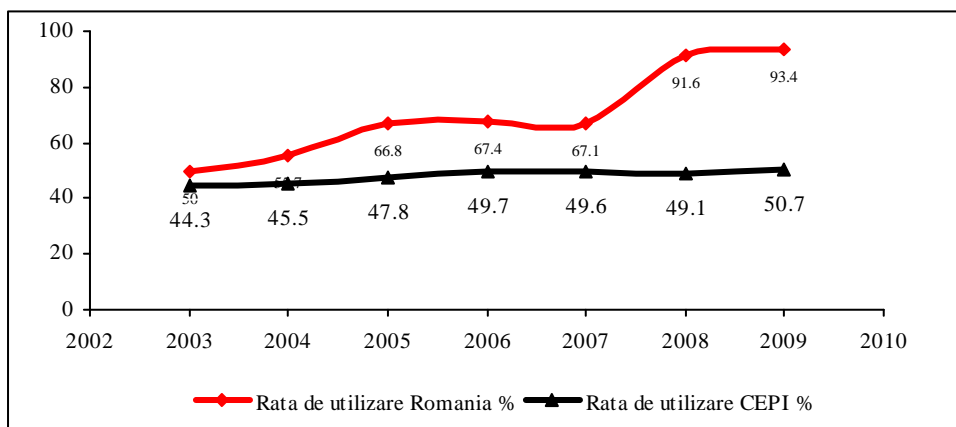


Fig. 4 Evoluția ratei de utilizare a maculaturii în general, comparativ cu rata de utilizare CEPI, în perioada 2003 – 2009

- Valoarea ratei actuale de utilizare de 92 – 93% se situează mult peste valoarea medie de cca 50% realizată de țările CEPI, care includ în programul lor de fabricație o gamă foarte largă de

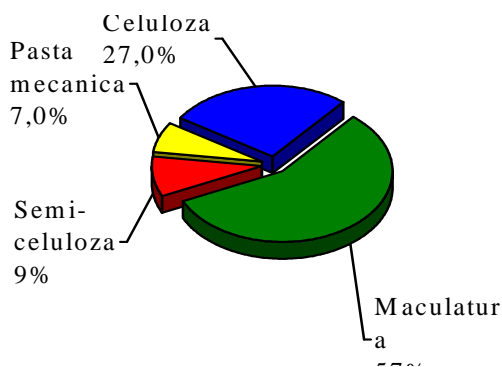
hârtii grafice și de alte sortimente superioare cu rate de utilizare a maculaturii scăzute, așa cum se poate constata din tabelul de mai jos:

*Tabelul 2 Utilizarea maculaturii în țările CEPI în anul 2009, la fabricarea diferitelor tipuri de hârtii și cartoane și gradul de utilizare a maculaturii*

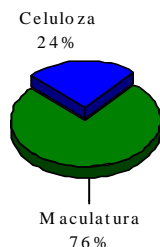
Produce papetare	Hartie de ziar	Alte hârtii grafice	Hartii miez / capac	Cartoane	Hârtii de ambalaj	Total hârtii de ambalaj	Hârtii igienico sanitare	Hartii tehnice și speciale	Total
<b>Grad de utilizare a maculaturii, %</b>	91,6	10,3	92,9	41,9	52,5	74,6	49,6	49,6	<b>50,7</b>

Sursa: Annual Statistic CEPI 2009

În figurile 5 și 6 se prezintă evoluția compoziției fibroase la fabricarea hârtiilor și cartoanelor în România, la nivelul anilor 2005 și 2009.



*Fig. 5 Structura compoziției fibroase la fabricarea hârtiilor și cartoanelor în anul 2005*



*Fig. 6 Structura compoziției fibroase la fabricarea hârtiilor și cartoanelor în anul 2009*

Comparativ cu anul 2001, producția de paste fibroase primare a cunoscut o scădere treptată, ajungându-se la începutul anului 2009 la sistarea completă a acesteia.

În cazul României, rata de reciclare are în prezent aceeași valoare cu rata de colectare, reprezentând cantitatea de maculatură valorificată prin reciclare, raportată la consumul total de hârtii și cartoane, dat fiind că reciclarea în Romania este în prezent singura formă de valorificare/reciclare a maculaturii.

În rata de reciclare este inclusă și cantitatea de maculatură livrată la export, pentru același scop de reciclare.

### Maculatura pentru ambalaje

În tabelul 3 se prezintă evoluția consumului de maculatură și a indicatorilor de reciclare a maculaturii pentru ambalaje realizați în perioada 2003 – 2009, iar în figura 7 se prezintă evoluția consumului de maculatură pentru ambalaje, comparativ cu evoluția consumului de maculatură în general.

Tabelul 3 Evoluția consumului de maculatură și a indicatorilor de reciclare a maculaturii

- mii tone-

Specificație	2003	2004	2005	2006	2007	2008	2009
Producția de hârtii, cartoane și confecții pentru ambalaje	226	222	215	220	237	227	158
Consumul de hârtii și cartoane pentru ambalaje	267	264	275	293	404	330	320
Maculatura colectată din ambalaje	115	151	147	156	203	196	195
Rata de colectare/reciclare %	43,1	57,2	53,4	53,2	50,2	59,4	60,9
Rata de utilizare, %	53,1	70,2	69,3	68,2	80,1	85,9	96,8
Obiectiv minim de valorificare prin reciclare pentru deșeuri din ambalaje de hârtii și cartoane, conf. HG 621/2005, %		12	15	15	15	60	60

Sursa:CEPROHART Brăila și ROMPAP

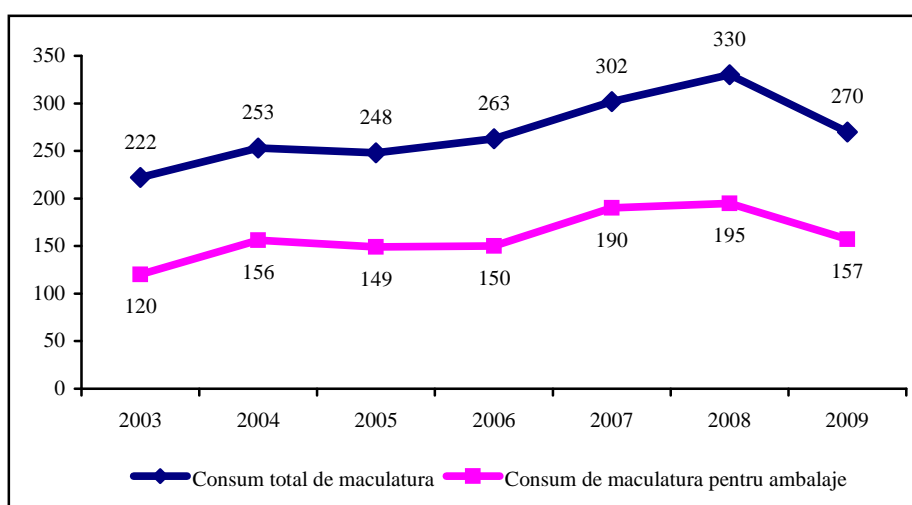


Fig.7 Evoluția consumului de maculatură pentru ambalaje comparativ cu evoluția consumului de maculatură în general

În figura 8 se prezintă comparativ, evoluția ratei de colectare/reciclare a maculaturii din ambalaje, față de evoluția ratei de reciclare a

maculaturii în general, în România, în perioada 2003 - 2009.

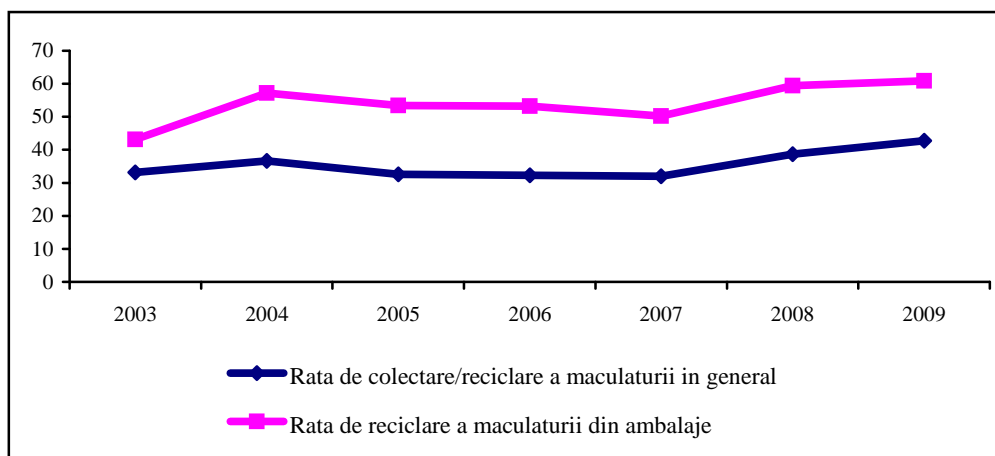


Fig. 8 Evoluția ratei de colectare/ reciclare a maculaturii din ambalaje față de rata de reciclare a maculaturii în general (%)

În figurile 9 și 10 sunt prezentate comparativ evoluțiile ratelor de colectare/reciclare și de utilizare pentru maculatura din ambalaje, comparativ cu ratele de colectare/reciclare și

utilizare realizate de țările CEPI, în perioada 2003-2009:

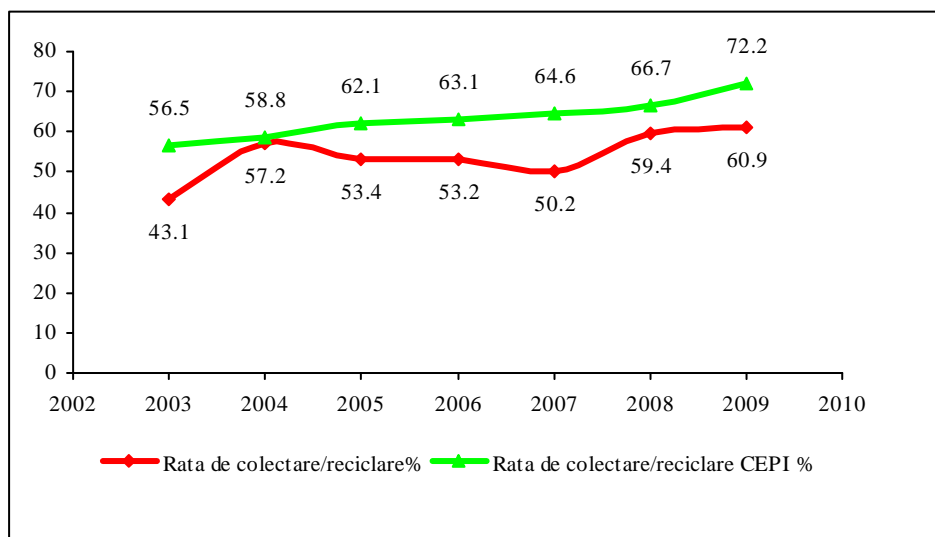


Fig. 9 Evoluția ratei de colectare/reciclare a maculaturii din ambalaje, comparativ cu rata de colectare/reciclare realizate de CEPI, în perioada 2003-2009

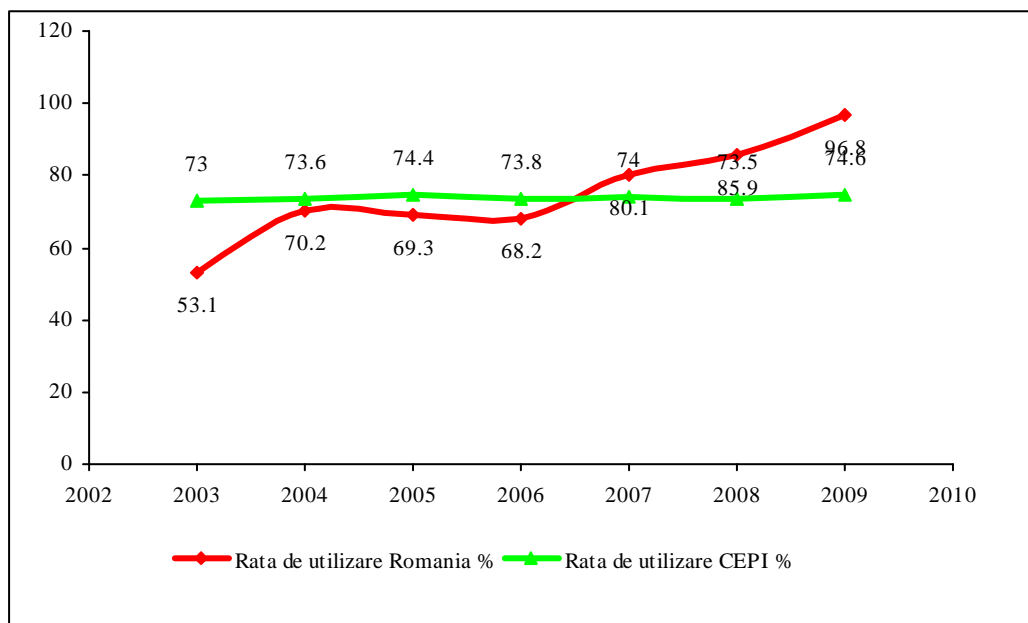


Fig. 10 Evoluția ratei de utilizare a maculaturii din ambalaje, comparativ cu rata de utilizare CEPI, în perioada 2003 – 2009

Comparativ cu datele prezentate la reciclarea globală a maculaturii, în cazul ambalajelor, ratele de colectare/reciclare sunt mai mari, datorită calității și selectivității maculaturii care se poate folosi la fabricarea ambalajelor, iar începând cu anul 2008 sunt la nivelul obiectivului minim de valorificare prin reciclare

pentru deșeurii din ambalaje de hârtii și cartoane conform HG 621/2005 modificată și actualizată de HG 1872/2006.

În anul 2009, s-a realizat obiectivul minim de reciclare a ratei de reciclare a maculaturii, respectiv cca **60,9%**, conform prevederilor HG 621 / 2005.

Se prezintă în figura 11 comparația între evoluția ratei de colectare/valorificare prin reciclare pentru maculatura destinată hârtiilor și cartoanelor de ambalaje, și valorile obiectivului

minim de valorificare prin reciclare impuse de UE.

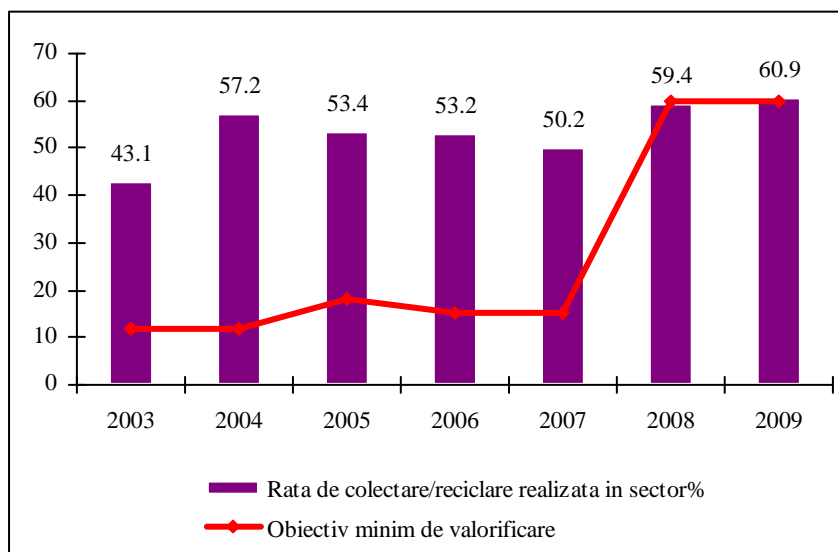


Fig. 11 Comparația ratei de reciclare a deșeurilor de ambalaje cu obiectivul minim de valorificare conform HG 621/2005

## II. Situația prognozată

### Proгноza consumului de maculatură și a indicatorilor de colectare, utilizare și reciclare a maculaturii

La evaluarea programului de producție de hârtii și cartoane, precum și a necesarului de paste fibroase primare și maculatură prezentat în tabelul 4, s-a avut în vedere:

- Reluarea creșterii economice a industriei din România după trecerea perioadei de criză, reluarea creșterii producției

interne de hârtii și cartoane, precum și o creștere a consumului de hârtii și cartoane, estimată la o rată anuală de 6%;

- Programul de producție prognozat al fabricilor din sectorul de celuloză și hârtie, la nivelul capacităților nominale de fabricație;
- Stimularea colectării maculaturii, a cărei rată medie de creștere anuală a fost estimată la cca 12% pe baza colectării separate de la populație, în principal;

Tabelul 4 Evaluarea programului de producție hârtii și cartoane și a necesarului de paste fibroase și maculatură

- mii tone -

Specificație	Realizat 2008	Realizat 2009	2010	2011	2012	2013	2014	2015
Producția de hârtii și cartoane	360	288	372	435	460	480	490	505
Consumul total de hârtii și cartoane	857	791	902	978	1022	1050	1080	1115
Consum intern de maculatura brută pentru hârtii și cartoane	330	270	340	407	430	450	460	475
Rata de colectare/ reciclare, %	38,7	41,0	42,8	44,0	47,0	51,4	55,5	60,5
Oferta de maculatură din țară (colectată)	332	324	386	430	480	540	600	675
Rata de utilizare %	91,6	93,4	91,4	93,5	93,5	93,7	93,8	94,0

Sursa: CEPROHART Brăila și ROMPAP București

În fig. 12 se prezintă evoluția estimată a producției și a consumului de hârtii și cartoane

în perioada 2008-2015, la nivelul țării.

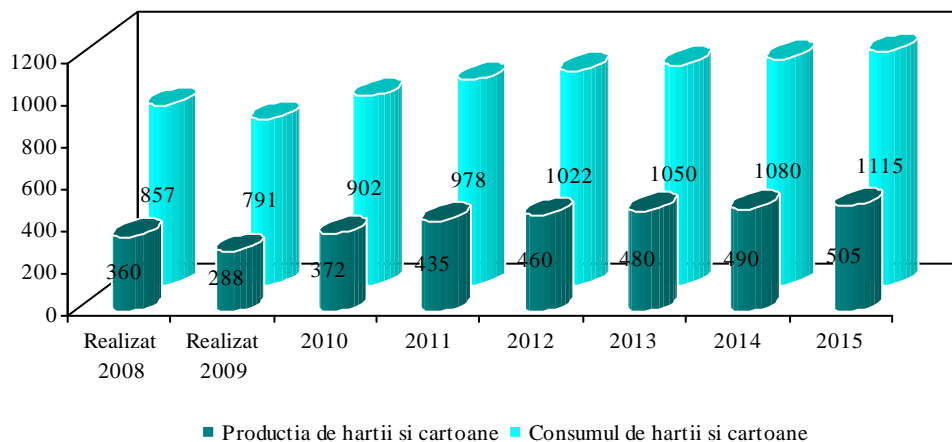


Fig. 12 Evoluția producției și a consumului de hârtii și cartoane în perioada 2008 – 2015

Evoluția estimată a ratei de reciclare a maculaturii din România, calculată în tabelul 4, se prezintă comparativ cu rata de reciclare din

țările CEPI, în figura 13. Se observă cum rata de reciclare din România se estimează că va avea o rată mai mare de creștere, dar în valoare absolută va fi sub valoarea obținută în țările CEPI.

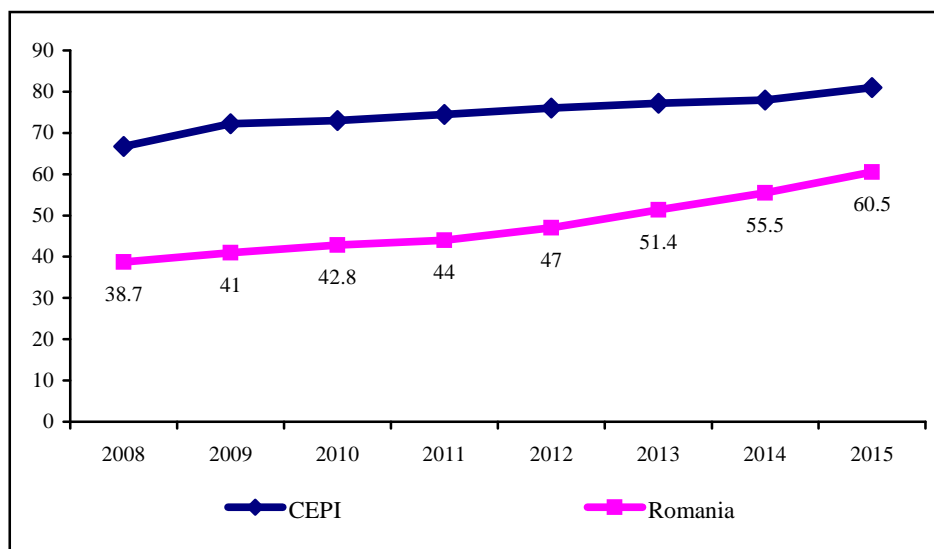


Fig.13 Evoluția estimată a ratei de reciclare a maculaturii din România comparativ cu cea estimată de țările CEPI

Astfel, rata medie de colectare a maculaturii în țara noastră va crește de la 41,0% în anul 2009, la 60,5% în anul 2015, apropiindu-se de ținta valorii Europene din anul 2010, care este de 66%.

Având în vedere structura de fabricație a sectorului de celuloză și hârtie, necesarul de

material fibros va fi constituit din preponderent din maculatură de pe piața internă și din celuloză, care se va importa în totalitate.

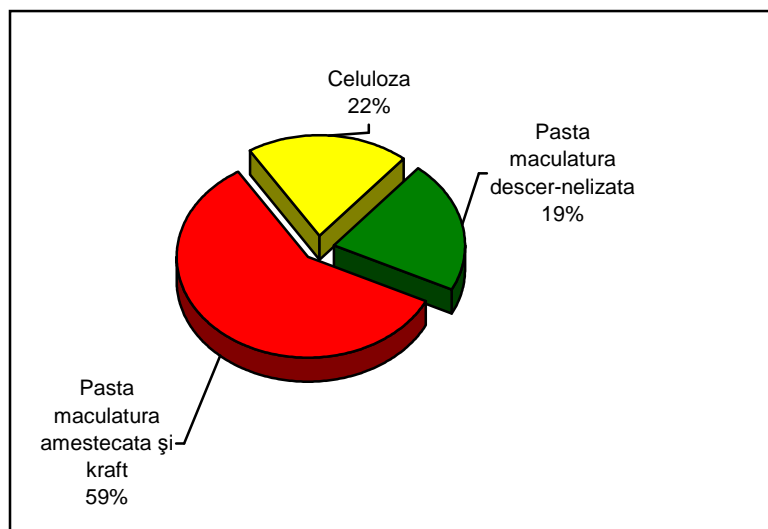
Celuloza va fi utilizată la:

- fabricarea hârtiei de ambalaj la SOMEȘ Dej;
- fabricarea hârtiilor tissue superioare la:
  - PEHART TEC Petrești;
  - COMCEH Călărași;

- MONTE BIANCO Târgoviște;
- VRANCART Adjud;
- fabricarea cartonului de transformatoare la PETROCART P. Neamț.

Structura fibroasă la fabricarea hârtiilor și cartoanelor preconizată pentru anul 2015, este prezentată grafic în **fig. 13**, cu următoarea distribuție:

- celuloză - 22%
- total pastă de maculatură – 78 %, din care:
  - pastă maculatură descernelizată – 21% (clasele III, IV și I)
  - pastă maculatură amestecată + kraft – 59% (clasele I +II)



*Fig. 13 Structura fibroasă estimată la nivelul anului 2015*

Gradele de utilizare a maculaturii pe sortimente vor fi următoarele:

- hârtii pentru carton ondulat (hârtii miez și testliner) – 100 %
- hârtie de ziar – **100%**
- hârtii igienico-sanitare – 56,2% în 2009, și 50,0% în 2015

- hârtia de ambalaj – **0%** în prezent și 25% din 2012
- carton triplex – **100%**

În tabelul 5 și figura 15 se prezintă estimarea raportului cerere/ofertă.

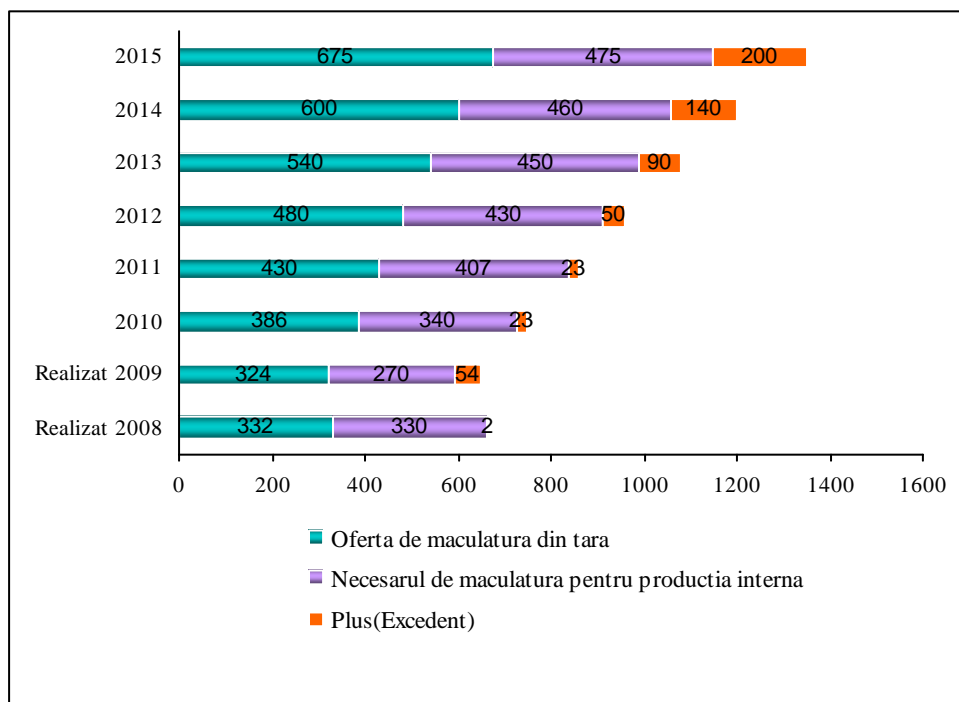
*Tabelul 5 Raportul cerere/ofertă maculatură*

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Indicatori	Realizat 2008	Realizat 2009	2010	2011	2012	2013	2014	2015
Oferta de maculatură din țară (colectată)	332	324	386	430	480	540	600	675
Necesarul de maculatură pentru producția internă	330	270	340	407	430	450	460	475
Plus(excedent)	+ 2	+ 54	+ 23	+ 23	+ 50	+ 90	+ 140	+ 200

Sursa : CEPROHART Brăila și ROMPAP București





Concluzia optimistă este că:

Oferta internă de maculatură va putea acoperi atât necesarul crescând de maculatură al sectorului papetar, cât și cererea crescândă la export.

### III. Implicațiile transunerii noii Directive cadru privind deșeurile asupra reciclării interne a maculaturii

Directiva cadru veche privind deșeurile 2006/12/CE a fost înlocuită cu o directivă nouă Directiva 2008/98/CE, pentru care termenul limită de transpunere în legislația națională este 30.12.2010.

Una dintre cele mai importante reglementări aduse de noua Directivă 2008/98/CE este prezentată în **Articolul 6, care definește încetarea statutului de deșeu:**

*Anumite categorii de deșuri încetează să mai fie considerate deșuri, în sensul articolului 3 punctul 1 în momentul în care au trecut printr-o operațiune de valorificare, inclusiv reciclarea și îndeplinesc o serie de criterii specifice, care urmează să fie definite conform următoarelor condiții:*

*(a) substanța sau obiectul sunt utilizate în mod curent pentru îndeplinirea unor scopuri specifice;*

*(b) există o piață sau cerere pentru substanța sau obiectul în cauză;*

*(c) substanța sau obiectul îndeplinesc cerințele tehnice pentru îndeplinirea scopurilor specifice și respectă legislația și normele aplicabile produselor; și*

*(d) utilizarea substanței sau a obiectului nu va produce efecte nocive asupra mediului sau a sănătății populației.*

### Încetarea statutului de deșeu pentru maculatură

Maculatura îndeplinește toate cele patru condiții pentru încetarea statutului de deșeu și se poate considera că își pierde statutul de deșeu din momentul în care se separă de alte tipuri de deșuri (plastic, sticlă, metale, lemn). Din acest moment **devine obligatoriu** ca toți ceilalți actori implicați în lanțul de valorificare (colectorii, valorificatorii, transportatorii) să respecte **principiul colectării separate**, în vederea **asigurării calității** cerute de sortimentele papetare în compoziția cărora va intra maculatura.

Așa cum se prezintă în figura 16, utilizatorii de hârtii și cartoane se pot grupa astfel:

- Industria, comerțul și instituțiile publice, care pot asigura o colectare separată, la sursă, efectivă și eficientă a diferitelor clase de maculatură;

- Populația, de la care, prin aplicarea sistemului de colectare separată la sursă, va rezulta maculatură în amestec, asimilată cu clasa I de maculatură, conform clasificării CEPI, și separat, vor rezulta alte deșeuri de plastic, sticlă, metale, lemn, etc.

În continuare, maculatura în amestec, respectiv clasa I, va putea fi utilizată la fabricarea hârtiilor și cartoanelor, ca atare pentru de sortare, în scopul asigurării calității optime a produselor papetare în compoziția cărora va intra, cu respectarea prevederilor SR EN 643/2003, respectiv a grupelor CEPI.

Prezentăm în figura 16 schema bloc a lanțului de producere și valorificare a maculaturii și posibilele puncte de acțiune a criteriilor de încetare a statutului de deșeu pentru maculatură.

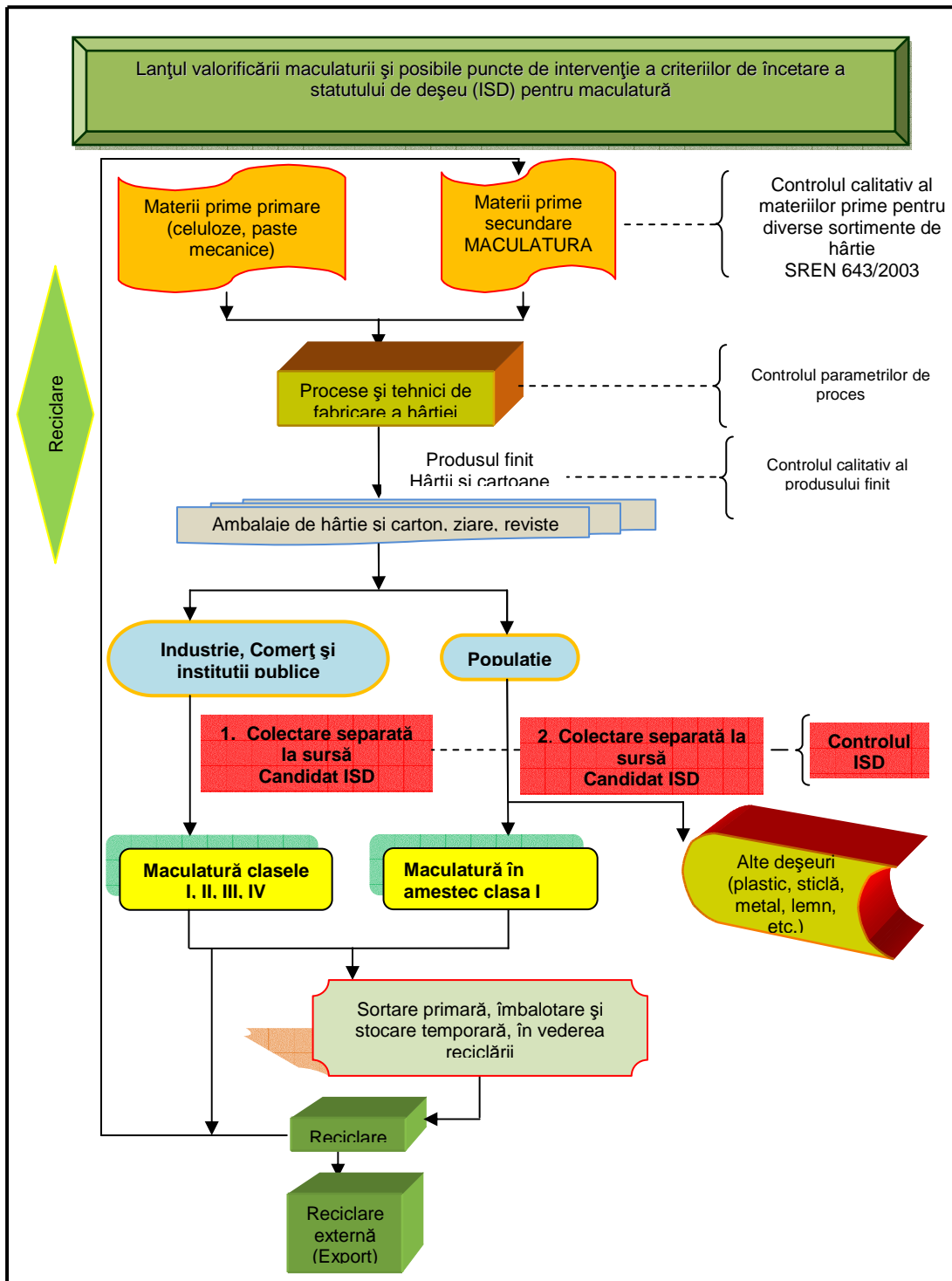


Fig. 16 Lanțul valorificării maculaturii și posibilele puncte de intervenție a criteriilor de încetare a statutului de deșeu (ISD) pentru maculatură

Prin implementarea prevederilor noii Directive-cadru 2008/98/CE referitoare la încetarea statutului de deșeu și prin impunerea obligativității colectării separate la sursă a maculaturii, se estimează următoarele **efecte benefice majore** pentru sectorul papetar din România:

- stimularea colectării maculaturii provenite de la populație, principala sursă potențială de maculatură, insuficient valorificată în prezent;
- creșterea cantității de maculatură disponibilă pe piață, pentru reciclarea atât internă, cât și externă, și cu posibilitatea reducerii prețului de achiziție a acesteia;
- îmbunătățirea caracteristicilor calitative ale maculaturii, diferențiat pe cele patru clase CEPI;
- asigurarea necesarului de maculatură pentru unitățile reciclatoare din cadrul sectorului papetar național, într-o măsură mai bună și la un nivel calitativ și de preț mai convenabil.
- stimularea circulației libere, neîngrădite, a maculaturii pe piața europeană, cu creșterea corespunzătoare atât a exportului, cât și a importului de maculatură;

#### **IV. Propuneri de măsuri/acțiuni pentru creșterea gradului de colectare, respectiv de reciclare a maculaturii, inclusiv prin crearea de operatori zonali de intermediere și centre de colectare a maculaturii proprii sectorului papetar**

În cadrul lucrării și în strânsă legătură cu contextul general al pieții de maculatură din România s-au analizat mai multe opțiuni privind îmbunătățirea organizării sistemelor de colectare, monitorizare și distribuție a maculaturii, în scopul unei mai bune asigurări a necesarului de maculatură din sector, cu accent pe următoarele două:

- Crearea de operatori zonali de intermediere, proprii sectorului de reciclare a maculaturii;
- Înființarea de centre de colectare și sortare a maculaturii, proprii unităților de reciclare din sector.

Din analiza tuturor aspectelor legale, economice și financiare, corelate cu posibilitățile și nivelul actual de cooperare între unitățile sectorului, rezultă că, la ora actuală, cea mai viabilă alternativă rămâne cea a înființării de centre de colectare și sortare a maculaturii, proprii

unităților reciclatoare, după modelul practicat cu succes de S.C. VRANCART S.A. Adjud, care, prin centrele proprii, își asigură în prezent cca. 35% din necesarul de maculatură.

Au fost identificate câteva obiective și soluții, care, prin implementare în diverse legi, planuri și programe, pot duce la intensificarea colectării separate a deșeurilor reciclabile și la reducerea generării de deșeurii municipale și similare celor municipale, conform DIRECTIVEI 2008/98/CE:

- **Investiții în infrastructura de salubritate** în vederea implementării colectării separate la sursă a deșeurilor în scopul reciclării/valorificării specifice a fiecărui tip de deșeu;
- **Implementarea obligatorie a colectării separate**, la sursă, a deșeurilor din toate localitățile, cu respectarea următoarelor condiții:
  - Organizarea colectării separate se va face pe principalele tipuri de deșeurii/materiale, respectiv hârtie, plastic, sticlă și metale;
  - Companiile de salubritate vor asigura:
    - containere speciale și/sau saci din plastic, separat pentru fiecare tip de material, funcție de condițiile diferite de amplasare;
    - amplasarea respectivelor containere/saci în apropierea locului de generare a deșeurilor, respectiv în spațiile disponibile din apropierea blocurilor, locuințelor, centrelor comerciale, de lângă piețele agroalimentare, instituțiile publice, etc.;
    - punerea la dispoziție a unui număr suficient de mare de containere și/sau saci funcție de populația deservită;
    - respectarea unui grafic ritmic de ridicare/golire a acestora;
- **Îmbunătățirea cadrului legislativ**, prin introducerea unor criterii clare de performanță în ceea ce privește serviciile de salubritate, cu accent pe îmbunătățirea accesului populației la infrastructura de **colectare separată** a deșeurilor;
- **Includerea unor sancțiuni severe** pentru serviciile de salubritate și societățile de colectare pentru nerespectarea

obligativității de colectare separată la sursă a deșeurilor, pe tot lanțul de colectare și reciclare, putându-se merge până la ridicarea autorizației de funcționare pentru aceste nereguli;

- **Creșterea nivelului de conștientizare și sensibilizare** a populației pentru punerea în aplicare a sistemului de colectare separată.

Au fost identificate de asemenea și diverse măsuri **ce pot fi luate la nivel legislativ, de administrația centrală, locală, sau de către instituțiile publice**, pentru prevenirea/minimizarea impactului generării deșeurilor de hârtii și cartoane:

- **Promovarea principiilor de eco-design**, respectiv de integrare sistematică a aspectelor de mediu în proiectarea ambalajelor din hârtii și cartoane, cu scopul de a îmbunătăți performanța de mediu a acestora pe toată durata ciclului de viață;
- **Proiectarea ambalajelor** astfel încât să răspundă cerințelor consumatorului, dar să fie cât mai puțin voluminoase, rezultând astfel un consum minim de resurse și implicit un volum minim de deșeuri;

- **Promovarea cercetării și a dezvoltării** în vederea realizării de produse papetare noi, prin aplicarea de tehnologii cât mai curate și mai economice, cu accent pe distribuția și utilizarea acestor rezultate;
- **Realizarea unor baze de date** privind tehnicile de prevenire a generării deșeurilor de hârtii și cartoane, în vederea implementării celor mai bune tehnici disponibile specifice sectorului papetar;
- **Stimularea producției de ambalaje** din hârtii și cartoane, care sunt deșeuri ușor biodegradabile, în detrimentul ambalajelor din materiale plastice, sau alte materiale nebiodegradabile.

## CONCLUZIE FINALĂ

Oferta internă de maculatură va putea acoperi atât necesarul crescând de maculatură al sectorului papetar, cât și cererea crescândă la export, cu condiția creșterii gradului de colectare a maculaturii de la populație, ca urmare a aplicării prevederilor noii Directive – cadru a deșeurilor și prin eforturile unite ale reciclatorilor de maculatură.

## PHOSPHONATES – ADITIVES FOR SOFTWOOD DELIGNIFICATION

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### Abstract

Taking in consideration that the penetration speed of the chemicals within the core of the wood chips are the determined stages of the impregnation and consequently to the increasing of the cooking yield and uniformity, the phosphonates influence regarding the reducing of the superficial tension of the cooking liquor within the wood chips capillaries become an research subject more and more actual. The great stability of the phosphonate in the sulphate cooking process, together with the great tensile surface reducing led to its choose for laboratory testing phase. The increase of the cooking uniformity by reducing the screening rejects to the half, and increasing cooking yield values with more than 4 units demonstrate the potential of this type of additives on pulping process.

**Key words:** *Phosphonates, Cooking, Chemical Pulp, Yield*

### Rezumat

Viteza de penetrare a chimicalelor în tocătura din lemn este determinată de fazele de impregnare și are ca rezultat creșterea randamentului și uniformității procesului de fierbere. La ora actuală, utilizarea fosfonaților cu efect asupra reducerii tensiunii superficiale a leșiei de fierbere în interiorul capilarelor tocăturii din lemn, a devenit un subiect de cercetare tot mai mult luat în discuție. Stabilitatea ridicată a acestor compuși în procesul de fierbere sulfat, alături de reducerea accentuată a tensiunii superficiale, au constituit argumente pentru testarea lor în fază de laborator. Creșterea uniformității procesului de fierbere prin reducerea refuzului la sortare, pe de o parte, și creșterea randamentului de fierbere cu peste 4 unități, demonstrează potențialul de utilizare a acestor aditivi în procesul de fierbere a tocăturii din lemn.

**Cuvinte cheie:** *Fosfonați, Fierbere, Celuloză, Randament*

## INTRODUCTION

### *1.1 Overview of Reactions during Kraft Pulping*

The course of dissolution of lignin and carbohydrates reveals three distinct phases of a Kraft cook: *initial*, *bulk*, and *residual* delignification which affects the single wood components as summarized in figure 1 [1].

- *Initial phase:* the initial stage is characterized by losses in the carbohydrate fraction, which is more pronounced for hardwoods as compared to softwoods [2].

The hemicelluloses undergo deacetylation and physical dissolution, and peeling reactions also start. Cellulose degradation by peeling is negligible in terms of yield loss. Reactive phenol lignin units, such as a-O-4-ethers, are cleaved as early as the initial phase.

- *Bulk phase:* The core delignification occurs in the bulk phase and, importantly, both phenol and non phenol b-O-4-ether bonds are cleaved. About 70% of the lignin is removed. The reactions of the carbohydrates are characterized by secondary peeling (i.e., alkaline cleavage

- of the glycoside bonds), but also by stopping reactions, which are favored at elevated temperature. Methanol is liberated from 4-*O*-methylglucuronic acid side chains, and hexenuronic units are formed.
- *Residual phase*: the residual phase begins at a delignification rate of about 90%.
- carbohydrate losses.
- Delignification has slowed down considerably due to depletion of reactive lignin units. It is believed that the chemical nature of the residual lignin hampers further degradation reactions. A slow delignification is accompanied by rapid carbohydrate degradation, causing disproportionate.

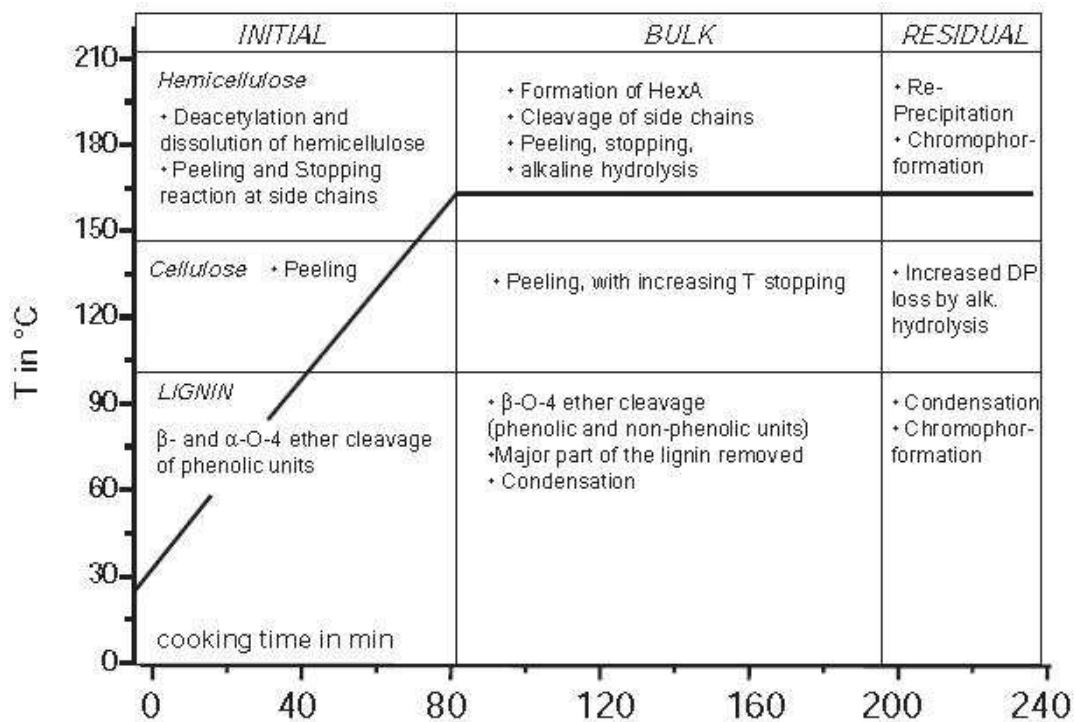


Fig.1 Phases of delignification and respective reactions of wood components

The initial stage is characterized by a substantial loss of carbohydrates, small but rapid delignification and high alkali consumption. In the second stage – generally referred to as the bulk delignification – the main dissolution of lignin takes place and the amount of carbohydrates and the alkali concentration in the cooking liquor decrease only slightly. Reaching a certain degree of delignification, the continuation of the cook results in the residual delignification phase

where the degradation of carbohydrates, mainly cellulose, predominates. The low selectivity in the final phase of a conventional Kraft cook is a limiting factor, as both the yield loss and the molecular weight degradation of cellulose are unacceptable. Consequently, the cook should be interrupted before the residual phase is attained. Figure 2 shows the course of delignification and carbohydrate degradation during alkaline pulping of beech (*Fagus sylvatica*) and spruce (*Picea abies*).

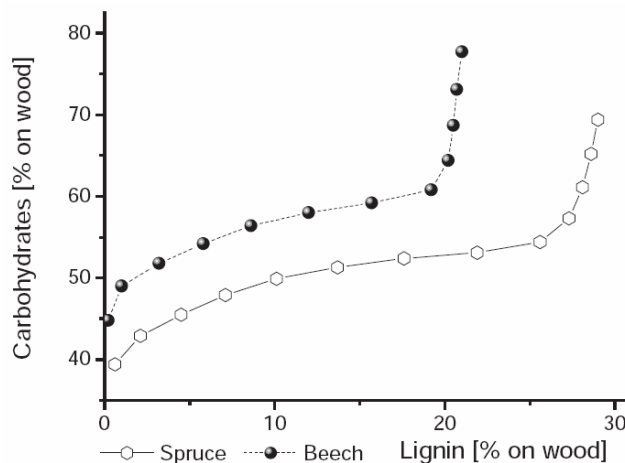


Fig. 2 Yield of total amount of carbohydrates as a function of the amount of lignin during alkaline pulping of spruce and beech at a liquor-to-wood ratio of 4:1; an EA-charge of 20.6% on wood; Results from Masura [3].

An increase in the process temperature in the range below boiling point under constant pressure was found to increase the rate of liquid penetration, which was attributed to a reduction in liquor viscosity [5, 6]. However, the higher temperature may have some negative effects on the penetration, including thermal expansion of the gaseous mixture within the wood chip voids and reduced solubility of air in the liquor. Lower surface tension caused by the higher temperature will

also improve the penetration process. In addition, the temperature of penetrating liquid may influence the penetration process by promoting changes within the capillary structure of wood chips [6] and affecting the swelling process [7]. The overall effect of temperature on the penetration of liquid into wood chips would be strongly dependent on the type of wood chips, the liquid and the pressure applied.

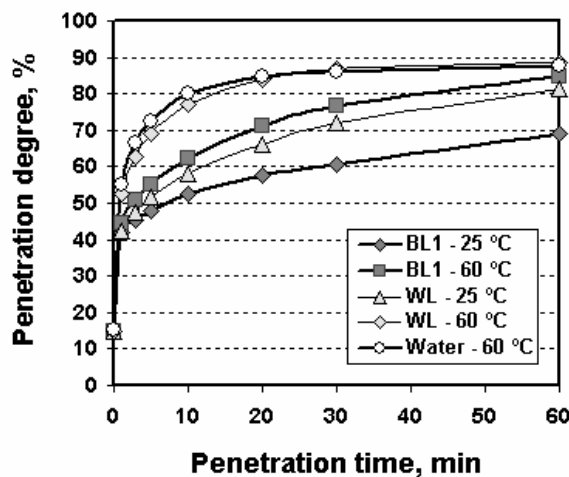


Fig. 3 Effect of temperature on penetration of cooking liquors into pine heartwood chips. Chip dimensions: 25x15x8 mm. Penetration over-pressure 5.3 bar.

Table 1 Liquid properties compared to the temperature increase

	Liquid	EA, g/l	DS, %	Viscosity, mPa		Surface tension, mN/m	
WL	White liquor	120	10	1.95 (25°C)	0.93 (60°C)	55 (25°C)	32 (60°C)
BL1	Black liquor	10	10	1.44 (25°C)	0.71 (60°C)	32 (25°C)	30 (60°C)
	Water				0.47 (60°C)		66 (60°C)

Under the boiling point the temperature increases have good influence regarding the

increasing of the chemical penetration speed into the wood chips capillaries, but if the

temperature increase the cooking selectivity decreases as it is shown in the table 2.

Table 2 Pulping selectivity denoted as the ratio of  $k_L$  to  $k_c$ . Kraft cooking of black spruce wood  $[OH]=1.1 \text{ mol L}^{-1}$ , liquor-to-wood ratio = 24:1; sulfidity = 30% according to [4] Li et al. (2002).

Temperature [°C]	$k_L^a$ [ $\text{kappa min}^{-1}$ ]	$k_c$ [ $\text{min}^{-1}$ ]	$k_L/k_c$
150	1.25E-04	6.70E-07	187
160	3.23E-04	2.14E-06	151
170	8.62E-04	6.79E-06	127
180	1.76E-03	1.72E-05	102

a) Apparent second-order reaction kinetics

Consequently, cooking at low temperatures makes it possible to extend Kraft cooking to lower kappa numbers without impairing pulp quality.

Therefore, reducing the surface tension create the conditions to manage the cooking process to the lower temperature, with effects on growth of yield and uniformity.

**Phosphonates**

Phosphonates as additives in alkaline cooking promise substantial energy savings, increased

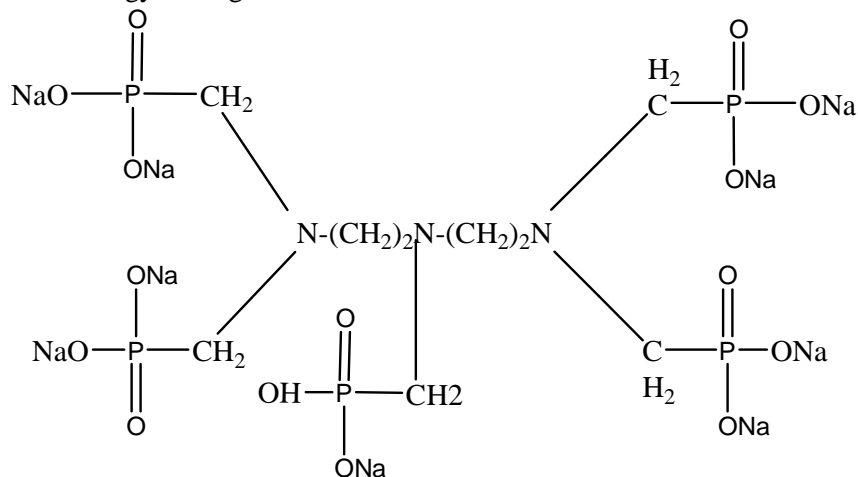


Fig. 4 Molecular structure of DTPMP-Na<sub>7</sub>

efficiency of delignification and bleaching cost reductions.

The chosen surfactant is DTPMP-Na<sub>7</sub> => C<sub>9</sub>H<sub>21</sub>O<sub>15</sub>N<sub>3</sub>P<sub>5</sub>Na<sub>7</sub> - the seventh sodium salt of the acid two-ethylene two-amino fifth-phosphorus.

It is presented in aqueous solution C = 25%, the molecular weight is 727 and the density of 1,38 g/cm<sup>3</sup>. The molecular structure it is presented in the figure 4.

**Applications:**

- Phosphonates can be added into the cooking liquor in the beginning of the Kraft cooking process to enhance lignin removal; the use of 0.1 - 0.3% phosphonate in the Kraft cooking process makes the degree of

- delignification sulfate more advanced by reducing the Kappa number
- Phosphonates may be used in all factories using alkaline cooking processes, because of it's stability to high temperatures and alkaline pH values



Other surfactants which can be used:

- DTPMA – acid two-ethylene three-amino fifth methylene phosphonate
- DEQUEST 2000 – acid three-amino methylene phosphonate -  $N(CH_2PO_3H_2)_3$
- DEQUEST 2006 – sodium salt of the acid amino methylene phosphonate –  $NaH[N(CH_2PO_3)_3]$
- BECLEN 633 – fifth sodium salt of acid two-ethylene three-amino fifth-methylene phosphonate, DETPMP,  $Na_5DTMPA$ ,  $M = 683$ ,  $d = 1,3$ ,  $pH = 6-8$
- DEQUEST 2066 – sodium salt of acid two-ethylene fifth-methylene phosphonate,  $Na_7H_3[(O_3PCH_2)_2NCH_2-CH_2N(CH_2PO_3)CH_2-CH_2-N(CH_2PO_3)_2]$ , USA Patent 7300542/2007

The installation used for the cooking trials is presented in the figure 5 bellow.

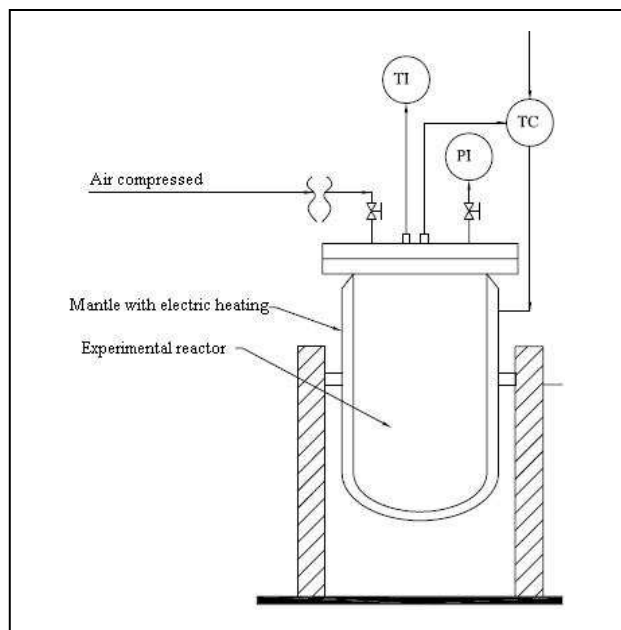


Fig. 5 Cooking installation used for trials

## EXPERIMENTAL

### Materials and methods

The materials used are detailed bellow:

1. DTPMP,  $c=25\%$  in aqueous solution
2. Spruce chips – industrial produced and screened as presented in the table 3

Table 3 Wood chips characteristics

Type of wood chips	Moisture	Density	Dimensions (mm)		
	%	kg/m <sup>3</sup>	Length	Width	Thickness
Spruce	16.83	140	22-35	20-25	3-5

3. White liquor with the characteristics shown in table 4.

Table 4 White liquor parameters

Parameter	Value	UM
Aa	97.6	g/l
Ae	88	g/l
At	123.2	g/l
NaOH	76.8	g/l
Na <sub>2</sub> S	19.2	g/l
Na <sub>2</sub> CO <sub>3</sub>	25.6	g/l
S	19.6	%
Density	1.112	g/cm <sup>3</sup>

Working conditions are detailed in the tables 5-8.

Table 5 Parameters for the study of phosphonate amount influence

Parameter	Value		
	1 h	1 h	1 h
Impregnation time	1 h	1 h	1 h
Cooking time	2 h	2 h	2 h
Impregnation temperature	115 °C	115 °C	115 °C
Cooking temperature	170 °C	170 °C	170 °C
Liquid-wood ratio	3 : 1	3 : 1	3 : 1
Active alkali adding (expressed in NaOH)	22 %	20 %	18 %

Table 6 Parameters for the study of temperature influence

Parameter	Value		
	1 h	1 h	1 h
Impregnation time	1 h	1 h	1 h
Cooking time	2 h	2 h	2 h
Impregnation temperature	115 °C	115 °C	115 °C
Cooking temperature	170 °C	165 °C	160 °C
Liquid-wood ratio	3 : 1	3 : 1	3 : 1
Active alkali adding (expressed in NaOH)	20 %	20 %	20 %

Table 7 Parameters for the study of duration influence

Parameter	Value		
	1 h	1 h	1 h
Impregnation time	1 h	1 h	1 h
Cooking time	2 h	1.5 h	1 h
Impregnation temperature	115 °C	115 °C	115 °C
Cooking temperature	170 °C	170 °C	170 °C
Liquid-wood ratio	3 : 1	3 : 1	3 : 1
Active alkali adding (expressed in NaOH)	22 %	22 %	22 %

- Kappa number
- Total yield (%)
- Amount of screening reject (%)
  
- Breaking length (Km)
- Burst index (kPam<sup>2</sup>/g)

Table 8 Parameters for the study of duration influence

Parameter	Value		
	1 h	1 h	1 h
Impregnation time	1 h	1 h	1 h
Cooking time	1.5 h	1.5 h	1.5 h
Impregnation temperature	115 °C	115 °C	115 °C
Cooking temperature	170 °C	170 °C	170 °C
Liquid-wood ratio	3 : 1	3 : 1	3 : 1
Active alkali adding (expressed in NaOH)	22 %	20 %	18 %

## RESULTS AND DISCUSSION

In order to conclude regarding the surfactant effects on cooking process, after the cooking, washing and pulp screening were made the following analyses:

<p>The reducing of surfactant amount down to 1% do not influence so much the pulp characteristics comparing to the blank trials, which means that there still are possibilities to reduce under 1% the adding of phosphonates without significant negative influences. Yet, the trials without additive shows higher increases in the reject amount and kappa number</p>	<table border="1"> <thead> <tr> <th>Results</th> <th>UM</th> <th>Values</th> </tr> </thead> <tbody> <tr> <td>Total yield</td> <td>%</td> <td>60.8 57.3 56.6 53.9</td> </tr> <tr> <td>Amount of screening reject</td> <td>%</td> <td>4.2 5.1 6.5 13.7</td> </tr> <tr> <td>Breacking length</td> <td>Km</td> <td>9.6 9.4 9.5 8.4</td> </tr> <tr> <td>Burst index</td> <td>kPam<sup>2</sup>/g</td> <td>3.2 3 3.3 4.1</td> </tr> <tr> <td>Kappa number</td> <td></td> <td>22 26 28.7 54.5</td> </tr> <tr> <td>Surfactant amount</td> <td>%</td> <td>3 2 1 0</td> </tr> </tbody> </table>	Results	UM	Values	Total yield	%	60.8 57.3 56.6 53.9	Amount of screening reject	%	4.2 5.1 6.5 13.7	Breacking length	Km	9.6 9.4 9.5 8.4	Burst index	kPam <sup>2</sup> /g	3.2 3 3.3 4.1	Kappa number		22 26 28.7 54.5	Surfactant amount	%	3 2 1 0
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<p>The reducing of the duration to the half shows that there still is possible to obtain pulp with good characteristics and relative high yield. The amount of 8.4% reject it is still acceptable.</p>	<table border="1"> <thead> <tr> <th>Results</th> <th>UM</th> <th>Values</th> </tr> </thead> <tbody> <tr> <td>Total yield</td> <td>%</td> <td>60.8 40.6 59.9</td> </tr> <tr> <td>Amount of screening reject</td> <td>%</td> <td>4.2 7.2 8.4</td> </tr> <tr> <td>Breacking length</td> <td>Km</td> <td>9.6 8.8 9.4</td> </tr> <tr> <td>Burst index</td> <td>kPam<sup>2</sup>/g</td> <td>3.2 3.3 4.1</td> </tr> <tr> <td>Kappa number</td> <td></td> <td>22 30.5 44.3</td> </tr> <tr> <td>Duration</td> <td>h</td> <td>2 1.5 1</td> </tr> </tbody> </table>	Results	UM	Values	Total yield	%	60.8 40.6 59.9	Amount of screening reject	%	4.2 7.2 8.4	Breacking length	Km	9.6 8.8 9.4	Burst index	kPam <sup>2</sup> /g	3.2 3.3 4.1	Kappa number		22 30.5 44.3	Duration	h	2 1.5 1
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<p>The reducing of the temperature shows that the increasing of the chemical diffusion speed by reducing of surface tension realized with this phosphonate clearly create the possibility to make thermal energy economy.</p>	<table border="1"> <thead> <tr> <th>Results</th> <th>UM</th> <th>Values</th> </tr> </thead> <tbody> <tr> <td>Total yield</td> <td>%</td> <td>60.8 58.9 59.9</td> </tr> <tr> <td>Amount of screening reject</td> <td>%</td> <td>4.2 5.1 5.7</td> </tr> <tr> <td>Breacking length</td> <td>Km</td> <td>9.3 9.1 9.4</td> </tr> <tr> <td>Burst index</td> <td>kPam<sup>2</sup>/g</td> <td>3.2 3.3 4.1</td> </tr> <tr> <td>Kappa number</td> <td></td> <td>22 34 43</td> </tr> <tr> <td>Temperature</td> <td>°C</td> <td>170 165 160</td> </tr> </tbody> </table>	Results	UM	Values	Total yield	%	60.8 58.9 59.9	Amount of screening reject	%	4.2 5.1 5.7	Breacking length	Km	9.3 9.1 9.4	Burst index	kPam <sup>2</sup> /g	3.2 3.3 4.1	Kappa number		22 34 43	Temperature	°C	170 165 160
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<p>Reducing the alkali amount down to 18% has no negative but positive influence regarding all the pulp characteristics. Taking in consideration that the trials were made at a cooking duration of 1.5 hours, good influence of DTPMP-Na<sub>7</sub></p>	<table border="1"> <thead> <tr> <th>Results</th> <th>UM</th> <th>Values</th> </tr> </thead> <tbody> <tr> <td>Total yield</td> <td>%</td> <td>40.6 50.8 56.5</td> </tr> <tr> <td>Amount of screening reject</td> <td>%</td> <td>7.2 7.3 7.8</td> </tr> <tr> <td>Breacking length</td> <td>Km</td> <td>8.8 9.2 10.3</td> </tr> <tr> <td>Burst index</td> <td>kPam<sup>2</sup>/g</td> <td>3.3 3.7 4.7</td> </tr> <tr> <td>Kappa number</td> <td></td> <td>30.5 44.1 48.6</td> </tr> <tr> <td>Active alcali amount</td> <td>%</td> <td>22 20 18</td> </tr> </tbody> </table>	Results	UM	Values	Total yield	%	40.6 50.8 56.5	Amount of screening reject	%	7.2 7.3 7.8	Breacking length	Km	8.8 9.2 10.3	Burst index	kPam <sup>2</sup> /g	3.3 3.7 4.7	Kappa number		30.5 44.1 48.6	Active alcali amount	%	22 20 18
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## CONCLUSIONS

The benefits of phosphonate using as additives are:

- Increasing the cooking yield with 4-6%
- Reduction of wood consumption with 8-12%
- Reduced consumption of cooking chemicals
- Reduces to the half the cooking duration
- Reduces cooking temperature, thus the thermal energy needed
- Improve the efficiency of liquor penetration in wood chips

Wood chips are much faster penetrated by the cooking liquor. These benefits are achieved by reducing the surface tension of chips pores, while reducing the links between lignin and cellulose fibers. Thus chemicals have easier access into the wood pores.

All these, results in a more uniform cooking and a growing amount of pulp obtained.

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## APPLICATIONS OF NANOPARTICLES IN THE WET-END CHEMISTRY

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### Abstract

The first part of the paper presents dissolved and colloidal substances at paper machine wet end, their classification and origin and influence over processes at paper machine wet end. The main aspects involved in the application of nanoparticles at paper machine wet end are reviewed further. The main types of nanoparticles used in paper making are described: colloidal silica, bentonite, micropolymers, aluminium based microparticles and cationic microparticles. Applications of colloidal silica in paper making are inclusively summarized. Thus the main action directions are shown: retention – dewatering- strength as well as effects that paper producer can manage in the field of improving paper sheet quality and making production costs more efficient.

In the second part the results obtained in the laboratory stage in the elaboration of an operational model of retention/dewatering polymer – modified bentonite and its transfer to industrial pilot are shown. Implementation of a polyacrylamide-modified bentonite retention system is quality paper making on a low speed Fourdrinier paper machine (90 m/min) has proved viable as regards machine functionality, quality characteristics of end product and economic efficiency.

**Keywords:** *Nanoparticles, Wet end, Bentonite, Retention, Dewatering*

### Rezumat

În prima parte a lucrării sunt trecute în revistă substanțele dizolvate, coloidale și disperse din partea umedă. Sunt prezentate substanțe dizolvate și coloidale formate în timpul fierberii, defibrării și din alte surse. În a doua parte a lucrării sunt prezentate rezultatele obținute în faza de laborator de elaborare a unui model operațional de retenție – deshidratare *polimer/bentonită modificată* și transferul acestuia în instalația pilot. Implementarea unui sistem de retenție pe bază de poliacrilamidă – bentonită modificată pe o mașină de hârtie cu sită plană de viteză redusă (90 m/min) s-a dovedit viabilă cu privire la funcționalitatea mașinii de hârtie, caracteristicile de calitate ale produsului și eficiența economică.

**Cuvinte cheie:** *Nanoparticule, Partea umedă, Bentonită, Retenție, Deshidratare*

## INTRODUCTION

The very complex nature of wet end chemistry, makes from this process one the greatest challenges for paper producers.

Chemical additives are directed towards the improvement of retention systems in order to decouple retention, dewatering and formation and, particularly, optimization of retention

programs selected for a certain mill according to the mill's specific conditions.

Another research challenge is the control of flocculation index and its effects in the production process. In conclusion, the flocculation monitoring systems and a deeper understanding of flocculation mechanisms, of flocculation and reflocculation kinetics as well the floc properties are still necessary.

Approached responsibly, the advanced processing of data and simulation programs are today tools, useful for process optimization, on-line monitoring and statistics.

Microparticle nanotechnologies in the nano field (1 – 300 nm) are proved able to provide responses and solutions to these challenges.

**Dissolved and colloidal substances at paper machine wet end**

*Classification and origin*

Anionic impurities usually consist in monomers, oligomers, polymers or hydrocolloids dissolved or colloidal. The origin of anionic impurities can be thus classified:

- Colloidal and dissolved substances built up during cooking or wood defibration.
- Colloidal and dissolved substances produced during pulp refining.
- Other process dissolved and colloidal substances (for instance in fresh water, additives and recycled fibres).

During the alkaline delignification lignin is splitted in low molecular weight fragments, and hemicelluloses are transformed up to simple hydroxiacids. These compounds are retrieved in white water at paper machine wet end in amounts that depend on washing, sizing degree and constructive elements of installation. A part of substances is dissolved during pulp refining (table 1) Products released during refining have much higher molecular weights, that present a significant importance as regards paper making chemistry because high molecular weight polymers have an enhanced ability to form complexes with cationic polymers.

*Table 1 Chemical composition of spent liquor from kraft cooking and dissolved substances during kraft pulps*

Kraft spent liquor	UM	Dissolved substances during refining	UM
Lignin	47%	Lignin	37%
Hydroxiacids	28%	Arabinose	3.6%
Formic acid	7%	Xylose	38.5%
Acetic acid	4%	Manose	1.8%
Extractible	5%	Galactose	3.2%
Others	9%	Glucose	2.8%
		Others	3.6%

Substances coming from fresh water may contain humus, surfactants, salines and of course, fungi, bacteria or algae. Additives used in paper making are an important source of dissolved and colloidal substances at paper machine wet end. They may come from water-repellent resins, starch used in mass or at surface in the sizing press, dry strength aids, wet strength aids, in dry condition and other operational process additives.

The influence of dissolved substances over processes at paper machine wet end has become more significant at the same time with closing the white water circuit and reducing fresh water consumption. Concentration of colloidal and dissolved substances in the white water circuits has increased significantly and in some cases, transported material becomes higher than that of fibres. Anionic polymers from wooden mass generally have a lower sorption capacity on fibres and as a result they will concentrate in white water circuit and will influence the paper making process ( table 2).

*Table 2 General effects of electrolytes and anionic polymers in paper making*

Specification	High content of electrolytes	High content of wood anionic polymers
Strength properties	-	+ hemicelluloses - lignin
Refining speed	-	0
Dewatering	+	-
Paper sizing	-	--
Fines retention	-	--

Generally speaking, hemicelluloses favorably influences interfibres bonding, compared to lignin that provides paper rigidity and the property of being brittle.

Anionic impurities react and inactivate cationic retention additives. In production systems with a high closing degree of white water circuits, cationic retention aids cannot be used without a preliminary inactivation of anionic impurities. High charge density cationic polymers that are used for the control of anionic impurities are commonly type epichlorhydrins, polyamidamines, polyethilenimines or polyDADMAC.

**Types of microparticles used at paper machine wet end**

**Colloidal silica**

The chemistry of producing and using colloidal silica is widely described by Iler in its paper in 1979 [1]. Shortly, colloidal silica is prepared by partial acidification of monomeric silicate alkaline solutions. Limiting acidification, by keeping the pH above the neutral point, silica dispersions are obtained, known as „sol silica”. The mixture ageing can result in increasing the particle size. In order to provide a permanent ionic charge to colloidal

silica that is pH independent, aluminum atoms were replaced in the colloidal solution. Due to the valence difference, a permanent anionic charge can be maintained, at an acid pH (figure 1).

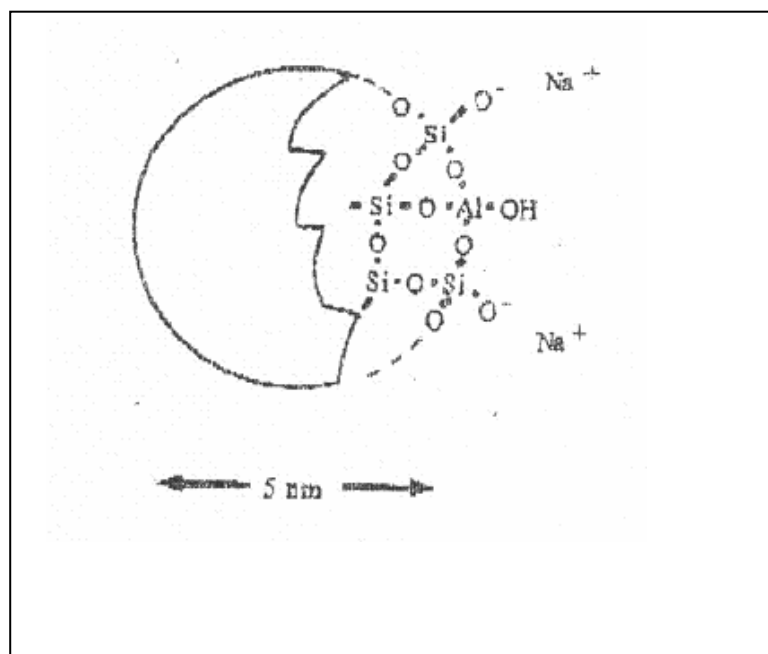


Fig. 1 Modified surface of colloidal silica

**Silica microgel**

The following development has been the rise of colloidal silica efficiency, by rising the surface and implicitly the anionic charge. It has been obtained by reducing the macromolecule dimensions from a diameter of around 5 nanometers, to a diameter ranged between 1 and 3 nanometers. Consequently, due to this significant reduction of macromolecule dimensions, this product is known as nanoparticles.

Moreover, colloidal silica had a structure as some discrete spheres, bonded in linear chains, that interact with starch. Modification of surface has been maintained, in order to enable this product to be used in paper making in acid or alkaline medium (figure 2).

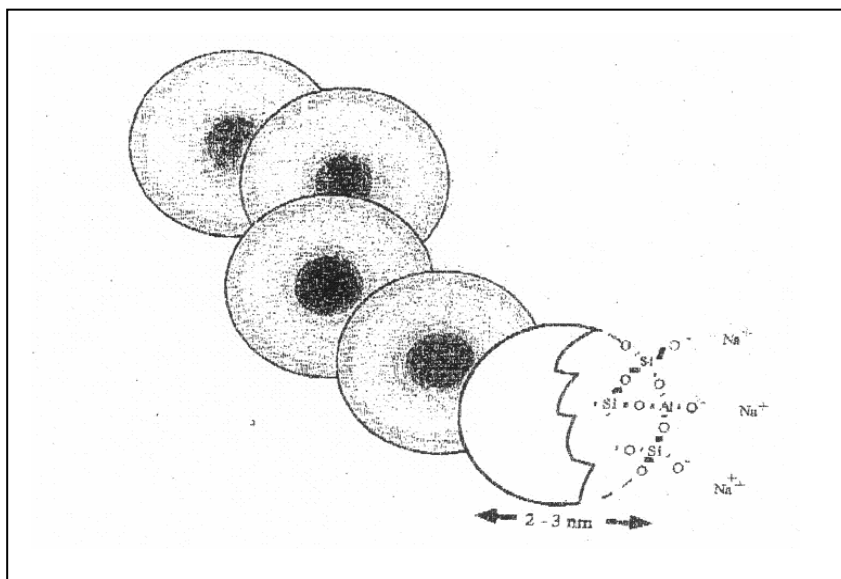


Fig. 2 Colloidal silica nanoparticles in the third generation

**Bentonite** (alkaline montmorillonite)

The commercial montmorillonite or „bentonite” particles have dimensions ranged between 1nm thickness and 300 nm length of flat surface. The actual thickness is often larger due to the incomplete delamination.

According to illustration in Figure 3, the montmorillonite particles can have forms that are quite different than colloidal silica. The common elements of the two types of microparticles are a high negative charge of the surface and a high specific surface on the mass unit.

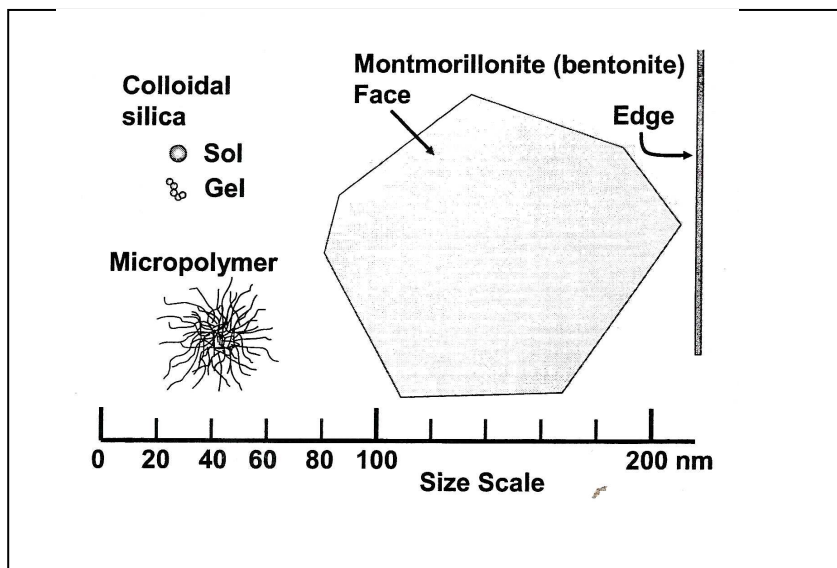


Fig. 3 Specific form and dimensions for colloidal silica, montmorillonite and micropolymers used as additives in dewatering systems

The first bentonite based dewatering and retention systems date back since the '80s [4] and used anionic non-ionic polyacrylamides or slight anionic charge. The study shows that the strength of interaction

between microparticles and high weight polymer has been favoured by the presence of calcium ions and a low charge density of the anionic polymer.

### Micro-polymers

As in the paper science and technology the importance and potential of colloidal silica and bentonite microparticle based systems have started to be noticed, one of the questions that were raised was: „Should the particles necessarily be inorganic?”. Therefore, procedures that consisted in adding a high molecular weight cationic polymer, followed by an intense shear hydrodynamic regime and then added an anionic polymer with a medium molecular weight ranged between 75.000 – 1.250.000 g/mol have started to be described. The tests carried out on the Britt Jar laboratory device suggested as main effect of such a system a faster dewatering. Using an anionic polymer with sulphonated groups emphasized benefits both in the field of dewatering and retention. **Micro-polymers** used in such programs have been described as having a diameter ranged between 30 – 90 nm and three-dimension form [5]. The paper stock treatment with a high molecular weight polyacrylamide, followed by the charge of an anionic “micropolymer” provide high efficiencies in line with the anionic component charge.

### Lignin based microparticles

Additive metering programs are described. They comprise the addition of a cationic acrylic copolymer, or a similar material, followed by the charge of a modified lignosulphonate [6]. Lignin can be described as a condensed phenolic product. It develops an anionic loading in process water due to the presence of sulphonic acid and carboxylic acid groups. It has been noticed that a product obtained from formaldehyde with the naphthalensulphonic acid salt has a similar potential with that of microparticles. This condensed product, known as „tannin aid” improves dewatering, retention and to smaller extent, fibre flocculation.

### Aluminium based microparticles

Aluminium sulphate was used as a dewatering aid since the earliest times of paper making. The high positive valence of alumina types, especially when paper is made

in acid medium, makes it a very efficient aid for the neutralization of negative colloidal surfaces and anionic polyelectrolytes in the paper stock.

The well-known strategy of using alau based microparticle technology is making microparticles „in situ” in the paper stock. The paper stock should be alkaline, the ideal pH being around 8.00.[7] In order to make the particles in-situ, the alau or aluminium polychloride is charged after the centriscreen. The optimum structure has been identified as being that containing around three OH groups at an Al atom, in line with the neutral formula  $Al(OH)_3$ .

The cationic potato starch based systems followed by an alau charge have a maximum retention efficiency at an pH close to 8.00.

### Ways of using colloidal silica nanoparticles in paper making

The diagram below illustrates only some ways wherein the nanoparticle colloidal system can be used as a tool to increase machine efficiency and paper and board quality but in any case there is not an exhaustive abstract of the techniques that can be implemented (figure 4).

The nanoparticle technology provides significant benefits for retention, dewatering and strength. It is a tool in paper making, limited only by imagination of paper producers [13].

A paper producer can obtain good results in making production costs more efficient through the optimization of one or several from the following effects: increase of filler content in paper sheet, increase of machine productivity (increase of paper machine speed), reduction of costs with the waste water treatment system, increase of wire and felt lifetime, reduction of specific material and additive consumptions.

In the field of paper quality, through a more uniform distribution of fibres, fillers, dye and operational additives (starch etc) paper producer can reduce the double sidedness effect, improve paper surface characteristics and internal strength.



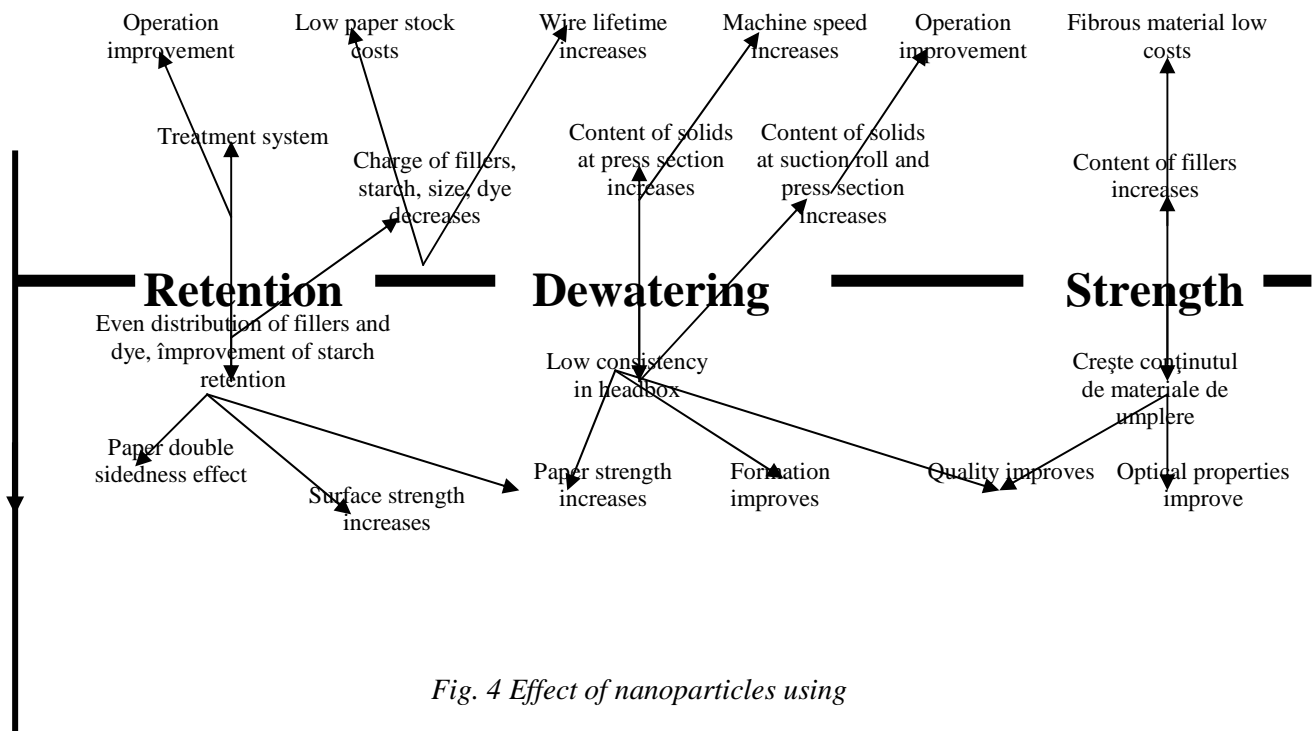


Fig. 4 Effect of nanoparticles using

## EXPERIMENTAL

### Objectives

- Elaboration of an operation model – formation/retention/dewatering technology in polymer-microparticle system of quality paper making on a low speed Fourdrinier paper machine;
- Estimation of impact over retention/dewatering/ formation at paper machine wet end;
- Estimation of quality performances of the paper produced in polymer-microparticle system.

Fibrous materials and additives used are shown in table 3.

Table 3 Fibrous raw materials and additives used

Material name	Characteristics	U.M.	Specifications
Bleached kraft softwood pulp	Brightness	%	83-84
Bleached kraft hardwood pulp	Brightness	%	85
Calcium carbonate – CaCO <sub>3</sub>	Average particle diameter	μm	4-6
	Brightness	%	91-94
AKD sizing aid	Ionic character		Very cationic
Optical brightener – IO	Substantivity		Good
PA retention aid	Appearance		Yellow, clear liquid
	Chemical nature		PA aqueous solution
	Ionic character		Cationic
	Solubility		It is diluted in any proportion with water
PAA retention aid	Appearance		White microspheres
	Chemical nature		High molecular weight polyacrylamide
	Ionic charge		Cationic
Modified bentonite clay - BM	Appearance		Fine powder
	Chemical nature		Modified bentonite clay
	Moisture	%	10
	Ionic charge, as pulp stock		Anionic
	Brightness	% MgO	35

**Experimental techniques and devices used:**

**Refining** has been carried out in the Valley Hollander, under standard conditions, up to a freeness of 32°SR for hardwood pulp and 38°SR for softwood pulp.

**Filler retention efficiency** has been determined from paper ash content.

**Total retention** has been determined for the DDJ – Dynamic Drainage Jaar device

**Pulp dewatering capability** has been determined in dynamic conditions on the DDJ device.

**Experimental program**

Steady charges:

- Furnish : Hardwood pulp : 70% - refined at 32 °SR and Softwood pulp: 30% - refined at 38 °SR

- AKD: 1.3 %;

- IO: 0.3%;

Variable charges:

- CaCO<sub>3</sub>: - ver. I : 20% CaCO<sub>3</sub> in relation to b.d. fibre

- ver.II : 40% CaCO<sub>3</sub> in relation to b.d. fibre

- PAA: 0.03% and 0.06% charges;

- BM: 0.1%, 0.25% and 0.50% charges.

Reference sample:

- The Reference samples have been considered furnishes with PA liquid retention aid charge of 0.25% and furnishes with 0.03% and 0.06% PAA charges without modified bentonite charge.

Charge order of additives in pulp slurry in homogenizer: AKD size⇒ CaCO<sub>3</sub> ⇒ IO

**Laboratory results**

Values determined for physico-mechanical characteristics, total retention, filler retention and dewatering capability, as well as comments concerning the flocculation character on the Rapid-Kothen sheet former, are shown in tables 4 and 5.

In figures nos. 5-6, evolutions of retention at first pass on the wire and stock dewatering capability with the PAA charge in the range of 0 – 0.06% and BM charge in the range of 0 – 0.5% are represented graphically.

The modified bentonite charge has a slight improvement effect both of total retention efficiency at first pass on wire and filler retention with an optimum effect for a 0.25% BM charge (figure 5).

The modified bentonite charge has an improvement effect of the stock dewatering capability being much better emphasized in case of a 20% calcium carbonate charge in relation to b.d. fibre (figure 6).

As regards formation, a fluffier structure is registered for the paper sheet prepared in the PAA - BM system proven by decreasing the paper sheet density and a slight decrease of the values determined for Gurley porosity (s).

Table 4 PAA – BM retention system; Filling (ver. I) : 20% CaCO<sub>3</sub> in relation to b.d. fibre

Sample codification	M0 (reference sample)	M01	M02	M11	M12	M13	M21	M22
<b>Variable charges :</b>								
- PAA,%	-	0,03	0,06	0,03	0,03	0,03	0,06	0,06
- BM,%	-	-	-	0,1	0,25	0,5	0,1	0,25
- PA,%	0,25	-	-	-	-	-	-	-
<b>Physico-mechanical characteristics</b>								
Basis weight, g/m <sup>2</sup>	80,5	81,4	82,3	78,5	82,8	79,3	81,3	81,0
Density, g/cm <sup>3</sup>	0,71	0,64	0,62	0,65	0,65	0,64	0,57	0,58
Gurley porosity,s	35/34	16,4/15,6	16/15,2	18,9/18,4	17,9/17,2	15,2/14,4	9,2/8,9	6,1/5,4
Breaking length, LR,m	5670	4550	4200	4760	4380	4090	3780	3450
Tear strength, mN	520	530	510	520	520	450	490	480
Burst strength,KPa	235	230	230	225	235	235	230	230
GA,%	88,9	88,4	89,6	88,4	89,0	88,2	90,7	89,9
Opacity,%	88,6	91,7	90,8	92,3	92,8	89,9	89,0	89,0

*Table 4 (continuation)*

Cobb absorbancy, g/m <sup>2</sup>	22/22	19/22	19/19	18/19	19/21	18/23	19/20	22/22
Ash, %	9,15	13,23	15,37	14,43	15,67	14,42	15,95	15,92
<b>Retention efficiency</b>								
Filler retention, Ru,%	59,8	80,6	93,6	87,9	95,4	87,9	97,1	97
Total retention,Rt,%	86,3	90,8	94,6	90,9	93,3	92,9	94,7	94,5
<b>Dewatering capability</b>								
V15, ml	350	320	330	340	345	400	360	410
<b>Flocculation</b>	Normal	Normal	Over flocculation	Normal	Normal	Normal	Over flocculation	Over flocculation

*Table 5 PAA – BM retention system; Filing (Ver. II): 40% CaCO<sub>3</sub> in relation to b.d. fibre*

<b>Sample codification</b>	M07	M03	M04	M31	M32	M33	M41	M42	M43
<b>Variable charges:</b>									
- PAA,%	-	0,03	0,06	0,03	0,03	0,03	0,06	0,06	0,06
- BM,%	-	-	-	0,1	0,25	0,5	0,1	0,25	0,5
- PA,%	0,25	-	-	-	-	-	-	-	-
<b>Physico-mechanical characteristics</b>									
Basis weight, g/m <sup>2</sup>	80,8	82,9	82,7	83	81,1	78,8	81,4	80,8	82
Density,g/cm <sup>3</sup>	0,70	0,63	0,65	0,63	0,6	0,58	0,63	0,58	0,6
Gurley porosity,s	27/26	9/9	12/12	11/10	9/9	8/8	11/10	7/6	5/4
Breaking length, LR,m	4580	3750	3670	3610	3620	3110	3220	2780	2340
Tear strength, N	480	520	400	400	390	320	370	370	280
Burst strength,KPa	225	235	235	230	245	245	245	264	-
GA,%	88,9	91,1	91	90,9	90,2	90,7	90,9	90,9	91,4
Opacity,%	90,5	91,7	91,4	91,3	90,5	91,2	91,2	91,1	90,8
Cobb absorbancy, g/m <sup>2</sup>	27	18	18	24	23	25	22	23	-
Ash, %	16,81	23,4	26,0	24,61	24,12	24,44	26,84	25,92	25,16
<b>Retention efficiency</b>									
Filler retention ,Ru, %	59,5	82,8	92,2	87,1	84,4	86,5	95,0	91,6	89,1
Total retention,Rt,%	82,8	86,9	87,8	89,8	91,8	92,2	95,1	95,6	96,2
<b>Dewatering capability</b>									
V15, ml	305	330	285	315	355	345	350	440	375
<b>Flocculation</b>	Normal	Normal	Super flocculation	Normal	Normal	Normal	Super flocculation	Superflocculation	Superflocculation

Reference sample - PA charge: 0.25%

Ru – filler retention at first pass

Rt - total retention at first pass

**Development of physico-mechanical characteristics**

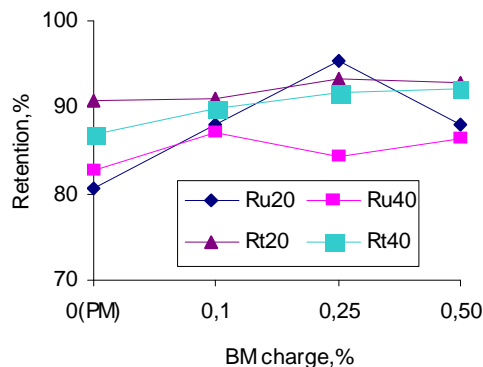


Fig. 5 Development of first pass retention with modified bentonite charge

PAA charge: 0.03% commercial product in relation to total b.d. material  
 Ru – filler retention at first pass  
 Rt - total retention at first pass  
 PAA charge: 0.03% in relation to b.d. material  
 CD – dewatering capability of the pulp filled with a 20 – 40% calcium carbonate charge in relation to b.d. material.

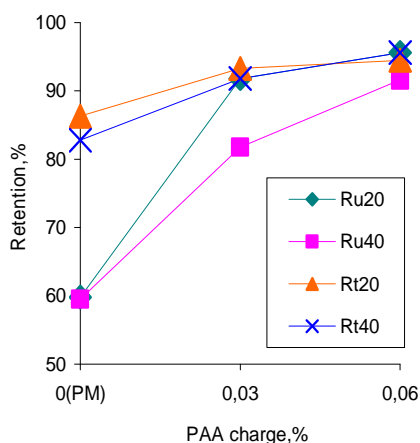


Fig.6 Development of first pass retention with PAA for the 0,25% BM charge

BM charge: 0.25% commercial product in relation to total b.d. material  
 PM: 0.25% CARTARETIN F charge  
 Ru – filler retention at first pass  
 Rt - total retention at first pass

Breaking length (m) and tear strength (N) are practically affected for 0.06% polyacrylamide charges and easily affected in case of a 0.5% modified bentonite charge. Increase of PAA charge to 0.06 % seriously affects the paper sheet appearance and a part of physico-mechanical characteristics due to superflocculation.

Burst strength improves both with the polyacrylamide charge ranged between 0 – 0.06% as well as the modified bentonite charge ranged between 0 – 0.5%.

Brightness and opacity of prepared sheets are not practically influenced by changing the retention system, the value determined being comparable with both the monopolymer retention systems and the polymer-microparticle retention systems.

Sizing efficiency remained at the same values or slightly improved if we consider the steady charge of size used and sensibly raised the ash content for the paper sheets prepared in the PAA – BM retention systems.

**Transfer of laboratory results to pilot level**

Following the analysis of laboratory results, a retention system with the following optimum coordinates has been recommended for the transfer to the pilot level, on a Fourdrinier paper machine, with an 1.6 m width and a speed of 70 – 100 m/min:

PAA charge: 0.03%;

BM charge: 0.25%

The charges concerned have been recommended for a calcium carbonate charge ranged between 20 – 40% in relation to b.d. pulp and a furnish made of:

- Bleached kraft softwood pulp : 30%;
- Bleached kraft hardwood pulp: 70%;

**Behaviour of the PERCOL – HYDROCOL retention system at paper machine wet end**

The PAA - BM retention system resulted in significant evolutions compared to the monopolymer system CARTARETINE F by means of the following parameters:

Less loaded primary circuit:

- White water consistency below the wire decreased from an average value of 0.124% to 0.030%;

- Launching consistency lowered from 0.57% to 0.43% mainly as a result of reducing water loading in the primary circuit;

Improvement of retention efficiency

- Retention efficiencies at first pass improved from 78.2% to 93.05% for total retention and from 50.7% to 71.8% for filler retention;

- Improvement of filler retention is reflected in decreasing the ash content in the launching stock from 34% to 22.2% .

Machine functionality

Machine had a very good operation during the demonstrative trial. Some breaks have registered at paper machine calender meaning a better operation compared to the previous reference period.

Quality characteristics of end product

Analysis of quality characteristics of end product reveals the following:

- Paper produced with the PERCOL – HYDROCOL retention system has a fluffier structure confirming that behaviour noticed in laboratory; therefore, paper density decreased from 0.74 g/cm<sup>3</sup> for the reference sample at 0.70 g/cm<sup>3</sup> and porosity increased sensibly, from average values of Gurley porosity of 16.1/15.8 s to 7.3/7.4 s;
- Smoothness of demonstrative sample had average values of 24/24 s compared to 33/29 s for the reference sample; registered decrease can be put on the fluffier structure;
- Average breaking length was 5430 m for the reference sample and 5260 m for experimental production and is within the variation regime of this characteristic for the same furnish and filling;
- Tear strength has registered a major rise, by around 31%, from 220/260 mN to 290/340 mN, beneficial to improve paper machine functionality;
- Ash content in paper sheet has been 12.1% for the reference sample and 12.3% for the experimental sample, proportional with the calcium carbonate charge metered at pulper;

Monitoring and analysis of parameters at paper machine wet end revealed that the polymer-microparticle retention system has a higher efficiency compared to the reference production in the monopolymer (polyamidamine) retention system through the following parameters: increase of retention efficiency at first pass, reduction of launching stock consistency, reduction of white water loading below the wire.

As regards quality characteristics, paper produced in the polymer - microparticle retention system had a fluffier structure, a lower smoothness and higher values for tear strength and dusting strength.

**CONCLUSIONS**

Implementation of a polyacrylamide-modified bentonite retention system in the quality paper making on a low speed Fourdrinier paper machine (90 m/min) is proved viable as regards the paper functionality, quality characteristics of end product and economic efficiency.

Monitoring and analysis of parameters at paper machine wet end has revealed that the polymer-microparticle retention system is efficient compared to the reference production in monopolymer (poliamidamină) retention system through the following parameters: increase of retention efficiency at first pass on wire, reduction of launching stock consistency, reduction of white water loading below wire.

As regards quality characteristics, paper produced in polymer-microparticle system had a fluffier structure, a lower smoothness and higher values of tear strength and dusting strength.

The economic analysis has emphasized the opportunity of obtaining savings even for an ash content in paper sheet of 12 %. Significant savings can be obtained (35-40 Eur/tonne) by rising the ash content in the paper sheet to 24-25%.

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**BOOK REVIEW**

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**CELLULOSE SCIENCE AND TECHNOLOGY**

2010, 368 pages, 16x24 cm, Hardcover, EPFL Press, ISBN 978-2-940222-41-4, CRC Press, ISBN 978-1-42000-6688-3

Cellulose represents the most widely spread organic polymer found in nature and it was used for a long time as a raw material for paper, textiles, film and flexible packing material. Due to its accessibility in huge amounts by photosynthesis process as a renewable material, cellulose is considered at present as a chance to answer to many problems connected with sustainable development. This explains the great scientific interest for this compound along with a lot of preoccupations to systematize the accumulated information in reviews and books. In the following, one of the last books dedicated to cellulose will be presented. In chapter 1, some general aspects concerning molecular structure of cellulose, along with its glucose monomer and related di- and polysaccharides such as amylose, chitin and chitosan are discussed. In the chapter 2 cellulose biosynthesis is described. This process which has been elucidated in the last years is comparatively analyzed in different organisms including plants and bacteria. It was established that cellulose biogenesis is a multi-step process involving terminal complexes containing cellulose synthase enzymes and spin cellulose microfibrils. The obtained information was made possible *in vitro* and chemical synthesis of cellulose. The structure and properties of cellulose are approached in the chapter 3. Having in mind aspects of molecular structure presented in chapter 1, the authors analyze supramolecular level of organization of cellulose. It is known that the properties of this polymer are influenced by crystalline structure which in the case of cellulose is different as a function of its polymorphs. Each polymorph is defined by its unit cell parameters determined by a special distribution of cellulose chains which influence the behaviour of the polymer. Further level of organization of crystals is into

microfibrils, layers or lamellae, cell walls, fibers, tissues or other morphological forms which are changed by the subsequent product processing. These aspects are discussed in the case of microfibrils, plant cell walls and bacterial celluloses related with biosynthesis processes. Cellulose is characterized by valuable mechanical and physical properties appreciated by its large scale utilizations. At the same time cellulose is biodegradable and non-toxic to living organism and interesting reinforced materials can be obtained using micro- or nanofibrils. Many aspects concerning utilization of cellulose are correlated with its swelling and dissolution, as resulting in chapter 4. The relationships between cellulose and water are very important in the processing, application, and storage of cellulosic materials which are discussed in term of intercrystalline swelling. This phenomenon is also characteristic when an interaction between cellulose and organic liquids take place. Intracrystalline swelling is induced by alkali metal hydroxides, salts in strongly alkaline solution, some inorganic acids, certain amines, ammonia and hydrazine. These problems are analyzed from the important applications point of view. Thus, dissolution is one of them, several proposals have been made and a variety of cellulose solvents already exist.

The dissolution of cellulose is discussed in detail and the possibilities of cellulose fibers obtaining are analyzed in the context of ecological problems along with increasing needs of fibers. Biodegradability of cellulose is determined by enzymes produced by some fungi and bacteria. This process is associated with carbon cycle in nature but its knowledge has a lot of advantages because both biodegradation and biostabilization of cellulose are important for some applications.

The enzymatic hydrolysis of cellulose represents the subject of chapter 5. The characteristics of enzyme and mechanism are very important for their applications. The peculiarities of enzymatic complexes are evidenced for different microorganisms including both fungi and bacteria, which are very important to develop genetic modification experiments and to obtain enzyme with specific activity for dedicated application. In the category of cellulose degradation are also included non-biological procedures presented in chapter 6.

The main reactions included are acid hydrolysis, alkaline degradation, oxidative degradation, thermal degradation, mechanical and radiation degradations which are very important for utilization, processing, stability and valorification of cellulose or lignocelluloses with the aim to obtain different chemicals. A lot of applications of celluloses refer to its derivatives. These are obtained from purified pulps using esterification, etherification, crosslinking and grafting (chapter 7). Taking into account the versatility of cellulose to be modified and valuable properties of cellulose derivatives, it is expected that their production will be developed in the future. Renewable resources defined as biomass are expected to be used to produce fuels and chemicals (chapter 8). There is a lot of information that demonstrates feasibility of different procedures based on biochemical or thermochemical conversion to solve the problems connected with the fuels and chemicals. At the same time, some processing steps may be implemented in integrated systems according to the new concept of biorefinery.

These possibilities are presented in optimistic view in the last chapter 9 (Perspectives) along with new tendencies of researches in the field of cellulose (biosynthesis, cellulose nanofibers, ionic liquid as new cellulose solvents). But successful solutions could be assured only by a large international cooperation between specialists from different fields and corresponding financial resources.

This book is presented in an excellent graphics and printed form and it will be useful to scientist and postgraduate students working in the field of cellulose and should be of interest for people working in the areas of complex processing of biomass.

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