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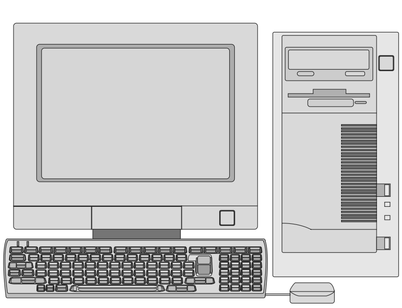

# ENERGY SAVING, INCREASING PRODUCTION CAPACITY AND QUALITY OF THE PAPER BY RECONSTRUCTION OF PAPER MACHINES

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### Abstract

Work is dealing with thermodynamic and hydrodynamic phenomena in paper production process in correlation with practical results obtained after reconstructions of commercial paper machines, in areas of constant part, press part and drying part. Here are shown present condition and condition after reconstruction of constant part, press part and steam condensing system. Also, the effects of the reconstruction of these three systems on paper machine are estimated from the point of energy saving, paper machine productivity and increasing of production capacity.
Obtained results prove that with relatively small investment great effects are achieved, and the investment is returned in few months, up to a year.

**Keywords:** Constant part, Press part, Steam condensation system, Syphons, Line pressure, Energy saving

### Rezumat

În lucrare sunt prezentate fenomenele termodinamice în procesul de producție a hârtiei în corelație cu rezultatele practice obținute după reorganizarea unei maşini de hârtie în partea preselor şi partea uscătoare.
Sunt prezentate rezultate comparative între starea actuală şi situația după reorganizarea părții constante a maşinii de hârtie, având în vedere economia de energie, productivitatea maşinii de hârtie şi creşterea capacității de producție. Rezultatele obținute demonstrează faptul că, cu investiții relativ mici, se realizează efecte mari, iar investiția se recuperează în câteva luni, maxim un an.

**Cuvinte cheie:** Partea constantă, Partea presei, Sistem de condensare abur, Economisirea energiei

## I. INTRODUCTION

The purpose of this work is to show possibility of reconstruction of paper machines with relatively small investment and notable effects in energy saving, increase of production capacity and paper quality. The results shown in this work are verified both by investors and engineers-authors of the work. The value of the work is its approach, starting from theoretic phenomena and laws and anticipating outcome of the reconstruction, which is verified through operational realization of project: from the value of investment to savings anticipated by given projects.

# 1. RECONSTRUCTION OF CONSTANT PART OF PM IN PAPER AND CARDBOARD PACKAGING FACTORY „LEPENKA“ NOVI KNEZEVAC

## 1.1. THEORY OF FINE CLEANING OF PAPER PULP

The purpose of the constant part of PM is reflected in following functions:

- removal of heavier, small impurities such as sand, glass, metal etc.,
- removal of lighter, small impurities such as crust, plastic, Styrofoam etc.,
- removal of the air from paper pulp,
- fine homogenization of paper pulp,
- acquiring stable, low concentration of paper pulp which is brought into feeding bed,
- removal of pulsations in the system for pulp feeding.

A number of devices are used for removal of previously stated impurities and execution of technology
functions, such as:

- vertical sorters, having holes with size 1-2 mm and slits with size 0,10 to 0,25 mm,
- vacuum systems such as deculator and various types of pipe cleaners.

Figure 1 shows schematic diagram of stated devices, which are built in the modern constant part for paper production. This work will primarily deal with pipe cleaners, for they were main target of the reconstruction of PM in LEPENKA.

**Pipe cleaners – devices for fine filtering of paper pulp on constant part**

Purpose of such devices is to perform fine cleaning of paper pulp of the sand, small plastic, hard parts etc. Various types of pipe cleaners are applied, giving various effects. Based on type and design of pipe cleaner there are variations in the effect of cleaning, pulp concentration, differential pressure (in-out), quantity of waste and electric power consumption of the pumps for pulp transport, figure 2.

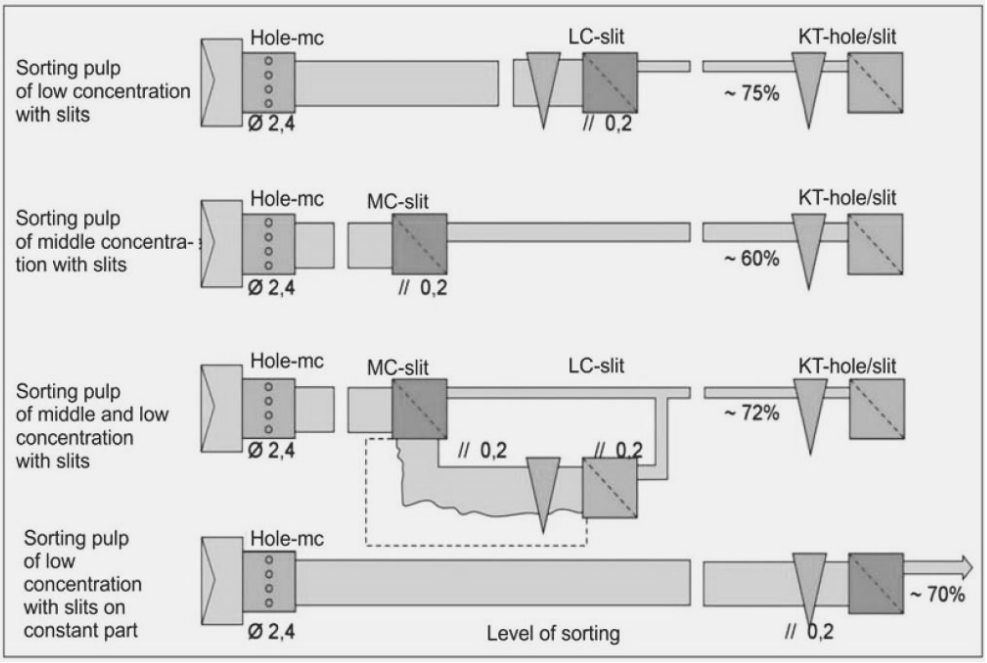


*Fig. 1 Systems for filtering paper pulp for packaging paper*

The working principle of pipe cleaners is shown in Figure 3. Paper pulp is fed tangentially into the head of pipe cleaner, with pressure of 2 to 4 Bar. Conical structure of pipe cleaner enables streaming of fed pulp under certain pressure and speed from head to the bottom of conical part of cleaner, where particles with greater specific weight are separated by the centrifugal forces and gathered on to the sides of cleaner, leaving it through the aperture as a waste. At the same time vacuum is created in the central part, collecting lighter impurities and moving them to the top of a cleaner. Fine pulp is retained in the middle of pipe cleaner and comes out purified at the head of pipe cleaner.

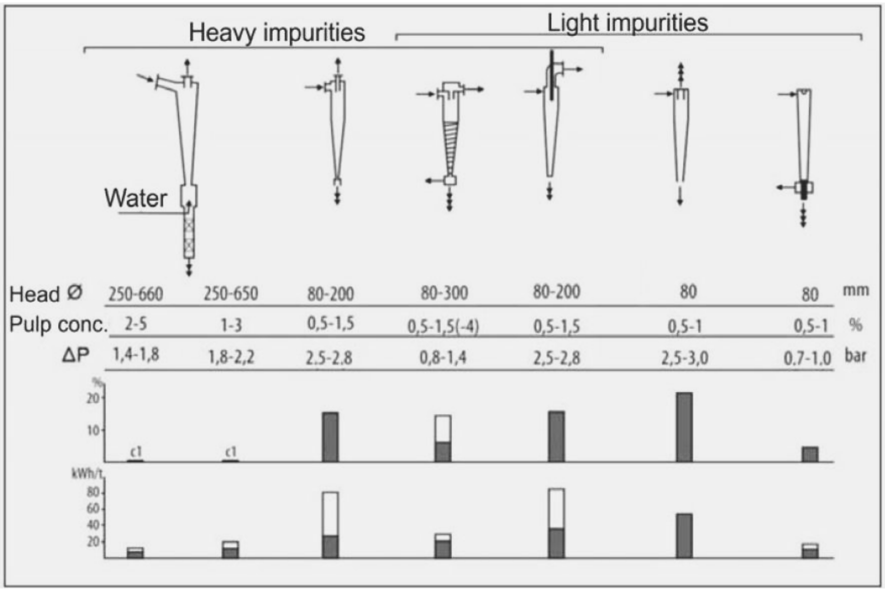


Fig. 2 Influence of the type of centricleaner on differential pressure, waste percentage and specific power consumption

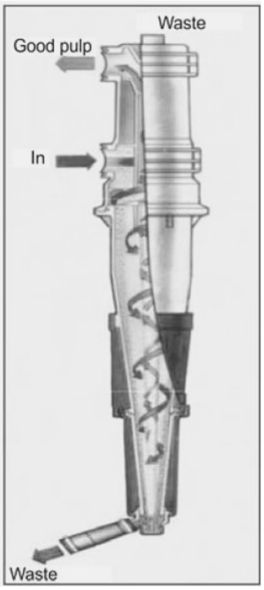


Fig. 3 Working principle of pipe cleaner

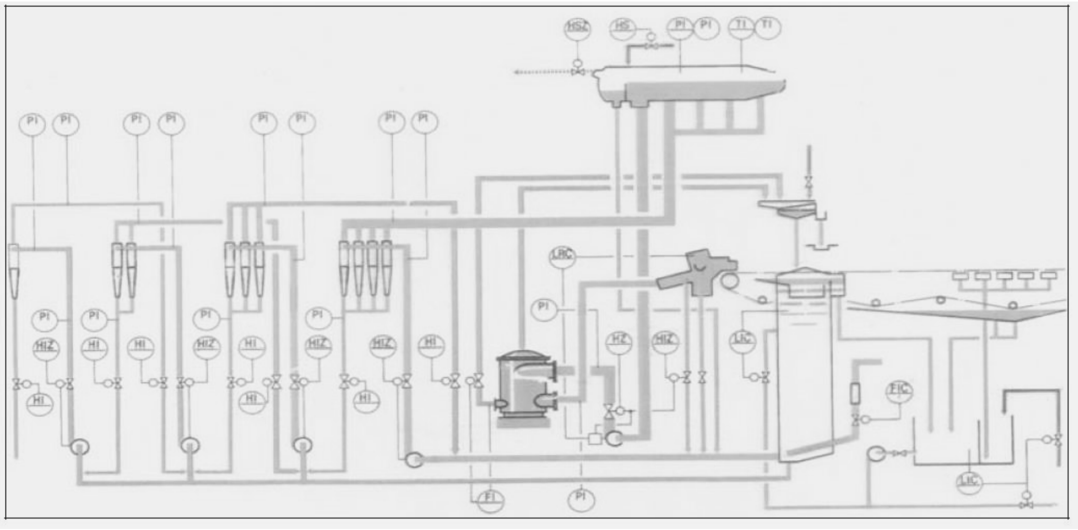


Fig. 4. Modern constant part with 4-level cleaning, deculator and two MIS pumps

## 1.2. HYDRO-DYNAMIC CALCULATION FOR CONSTANT PART OF PM

In order to correctly design constant part of PM, the following must be defined:

- PM capacity,
- paper sorts and weights,

In order to calculate pump capacity, engine power, diameter of pipes and necessary measuring and controlling devices, rigid standards must be applied, and such standards were honored here. In this work we will show part of reduced calculation which served as a basis for detailed designing:

- Working speed of PM, V = 250-300 m/min
- all technical and technological properties defining optimal running of constant part,
- retention of pulp on sieve,
- working principle of feeding bed and quantity of overflow,
- circular direction of pulp in constant part: MIS PUMP – feeding – MIS pump,
- properties of sieve water.
- Projected speed, V1 = 350 m/min
- Width of sieve, S = 2.850 mm
- Width of lane on roller, S1 = 2.570 mm
- Paper weight, g = 112 g/m2
- Retention on sieve, R = 70 %
- Daily production, q = 120 t/24h or 5,18 t/h

Target quantity of approx. 120t/24h demands approx. 12.000 liters of paper pulp per minute, with concentration of 0,8%.

How did we get this information?

**Supply of pulp to the feeding bed**

Quantity of pulp supplied to the feeding bed, i.e. quantity of pulp circulating in constant part is calculated this way:

$Q = S2 \cdot g \cdot R \cdot X \cdot V \cdot 60$, lit/min

where:

Q – quantity of pulp supplied to feeding system,
S2 – width of feeding opening, 2.750mm
g – paper weight, 112 g/m2
R – retention on sieve, 70%,
X – overflow and bypass in feeding system, 10% of total quantity of paper pulp,
V – working speed of PM, 300m/min

If we calculate with concentration of 0,8% in feeding system, then approx. 12.000 liters of paper pulp needs to be brought to feeding bed. Such quantity enables paper production of approx. 5,0t/h or 120 t/24h, giving net quantity of 100t/day..

In this calculation the standards for speed of fluids in pipelines from companies ANDRITZ AG, Graz and VOITH, St. Poelten, have been used, with following values:

- fresh water 3 to 3.5m/s,
- sieve water 2.5 to 3m/s,
- pulp with concentration up to 3% 1 to 2m/s
- pulp with concentration 3-5% 0.5 to 1m/s.
- pulp with concentration over 5% from 0.5m/s.

For the calculation of constant part, standards from company ANDRITZ AG – ESCHER WYSS for have been used for the assessment of pulp quantity in feeding bed, depending on sieve retention (Figure 5). Figure 6 shows the flow of paper pulp from feeding to roller, applied on PM in LEPENKA factory. Based on these standards and calculations constant part of PM in Lepenka was designed with precisely defined: properties of pumps, properties of engines, dimensions of pipeline, types of materials, number of pipe cleaners in 1st, 2nd and 3rd level of refining, properties of vacuum pump and properties of vertical sorters.

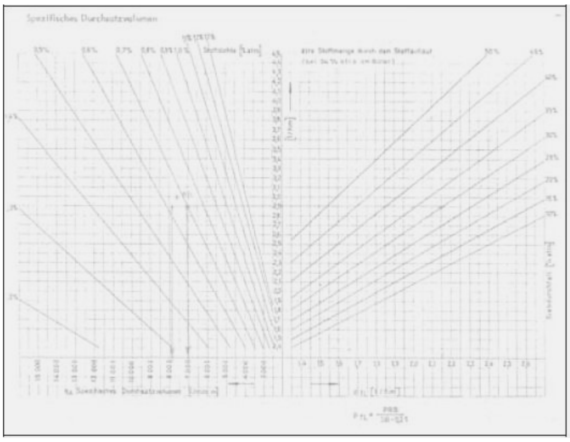


*Fig.5 Standard of ANDRITZ – ESCHER WYSS: determining pulp quantity in feeding System*

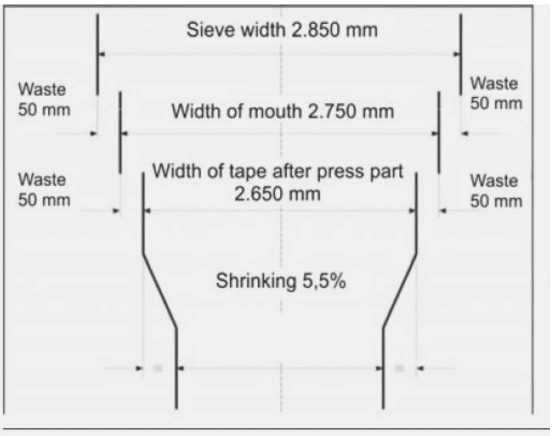


*Fig. 6 Scheme of the flow of paper pulp in LEPENKA, from feeding system, through sieve, press and drying part to roller*

## 1.3. CONSTANT PART – EXISTING CONDITION

Technological process of cleaning paper pulp in constant part of PM in LEPENKA proceeded as follows: paper pulp was transported from machine bed by the pump through regulator, with concentration of 3,5% into the leveling vessel. Next, pulp was transported by freefalling from the vessel to MIS pump over the regulation valve. Besides pulp, used water from sieve water pool 1, as well as refined pulp from vibration sieve was also conducted to MIS pump. Existing condition of the constant part of PM is given in Figure 7.

Diagram shows that the existing system was simple and unable to entirely perform all technological functions, stated above. The devices in this system operated as follows:

- MIS PUMP, capacity 17.300 l/min, height of water column 29m and engine power of

160kW, transported paper pulp with low concentration of 0.7-1.3%, through pipe cleaners with single level of cleaning, type BC, to vertical sorter and then into feeding bed;

- PIPE CLEANERS were technically designed to remove sand and heavier particles from paper pulp, but lighter particles remained in it;
- VERTICAL SORTERS, equipped with sieve holes 2.0mm large and rotor with 2 propellers, did not optimally clean paper pulp in this position, and rotor induced pulsations with amplitude up to 15mbar.

This had a negative impact on paper quality and deviation of weight in longitudinal direction.

*Deficiencies of existing constant part were following:*

- Poor cleaning of paper pulp, resulting in retaining light impurities, sand, glass etc. in paper.
- Poor visual appearance of paper,
- Inadequate quality of paper,
- Deviation of paper weight.

the recommendation was to install in this position modern vertical sorters with 6 or 8 propellers or with drum and sieve having perforations with slit dimensions 0.15-0.25mm or holes 1.2mm large, because those would perform optimal cleaning and amplitudes would not surpass value greater than 2.5mbar.

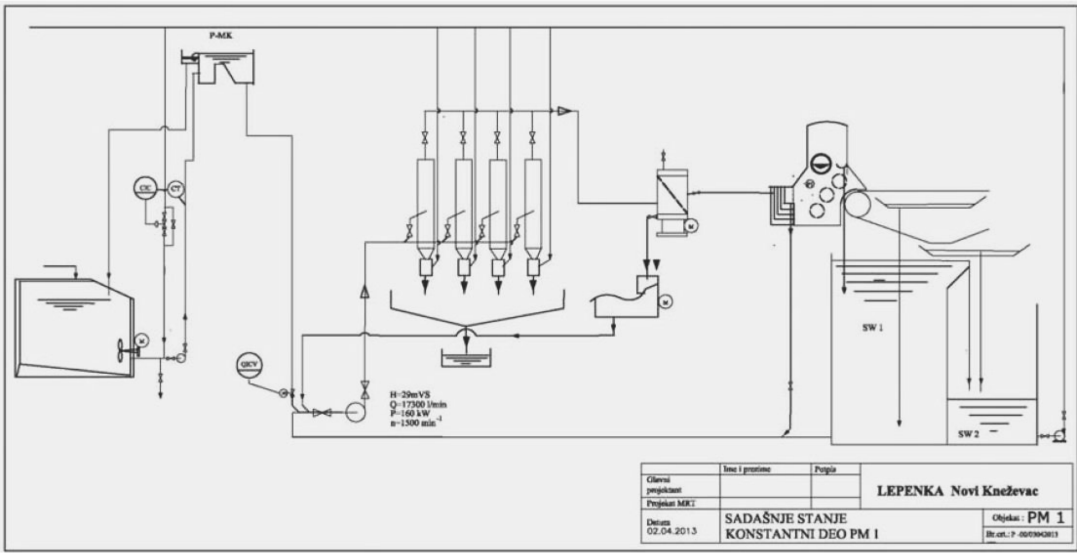


*Fig. 7 Present condition of constant part*

## 1.4. CONSTANT PART AFTER RECONSTRUCTION

After comprehensive analysis and studying knowledge in this field, three variants of constant part have been created, as follows:

1. variant with four levels of cleaning and two MIS pumps,
2. variant with three levels of cleaning and two MIS pumps,
3. variant with three levels of cleaning and one MIS pump.

Naturally, first variant with four levels of cleaning and two MIS pumps presented best solution from technological point; however in this phase of reconstruction its realization was unrealistic. Second variant was also discarded due to shortness of planned downtime of PM, and furthermore Investor did not have two pumps. For these reasons, third variant was chosen and used as a basis for the reconstruction, as shown in Figure 8.

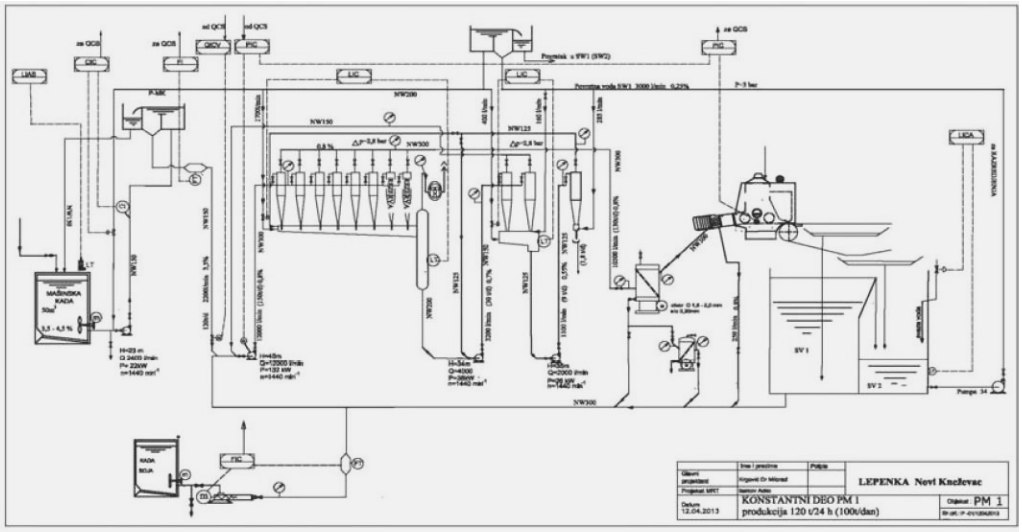


*Fig. 8 Constant part of PM with three levels of pipe cleaners and MIS pump, Variant 3*

## 1.5. PAPER SAMPLES, BEFORE AND AFTER THE RECONSTRUCTION

Here are shown pictures of paper samples – fluting, with weight 112 g/m2, produced from semi pulp made of straw (35%) and waste paper (65%), before and after reconstruction (Figure 9). It is noted that the paper sample before reconstruction contained various impurities, while sample after reconstruction is considerably more homogenous, with removed impurities.

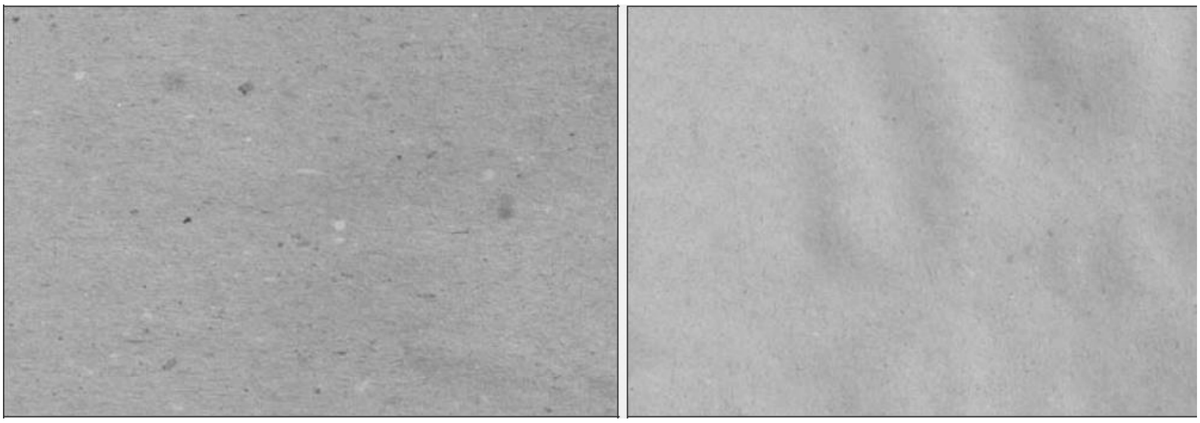


*Fig. 9 Samples of fluting paper before (left) and after reconstruction (right)*

**Evaluation of paper quality after reconstruction**

Figures given below are part of the Protocol signed between the LEPENKA factory as investor, and chief designer:

1. srenc, 110 g/m$^2$:
- visual appearance satisfying,
- mechanical properties – Mullen: before reconstruction: 160 kPa, after reconstruction:190 kPa.

2. fluting, 112g/m$^2$:
- visual appearance satisfying.
- mechanical properties, CMT: (due to inadequate quality of semi pulp made of straw, mechanical properties of paper before and after reconstruction can not be compared).

**General evaluation of the effects of reconstruction**

- Increase of the speed of PM 6,5%: from 235 to 250 m/min;
- Quality of srenc paper, Mullen: increase from 160 to 190 kPa;
- Quality of fluting paper, CTM: due to inadequate quality of semi pulp made of straw, mechanical properties of paper

before and after reconstruction can not be compared

- Removed sand and hard particles from paper pulp;
- Removed light impurities;

- For dissolution of pulp in constant part and regulation of concentration, sieve water (SV 1) is used instead of fresh water;
- Investment amount: symbolic, compared to the value of new foreign equipment;
- Executors of project: national experts.

### 1.6. CONCLUSION – ECONSTRUCTION OF CONSTANT PART

Based on received results after reconstruction of constant part of PM in Lepenka factory, Novi Knezevac, the conclusions are following:

1. visual appearance of paper is significantly better and meets the demands of the market, which was
the goal of reconstruction;
2. hard particles were removed from the paper;
3. reduced consumption of fresh water and increased utilization of raw materials;
4. improvement of mechanical properties of paper and capacity of PM has not been proven due to shortage of time and setting the production, but can be expected in reality;
5. complete reconstruction performed with domestic equipment, except second hand rollers for presses;
6. investment is approx. 8-10 times smaller than those for new equipment,
7. investment is returned in three months.

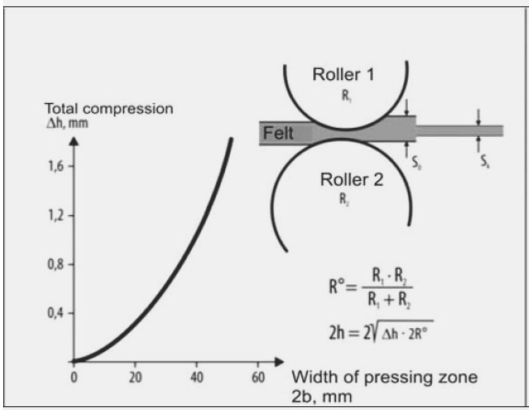


*Fig. 10 Dependence of pressing zone from diameter of rollers*

## 2. RECONSTRUCTION OF PRESS PART ON PM IN PAPER FACTORY „BEOGRAD“, BELGRADE

### 2.1. MATHEMATICAL MODEL OF THE PHENOMENON OF THE WATER REMOVAL IN PRESS PART

Commercial presses with contemporary contraction achieve dryness of paper tape of 54% before entering drying part, while experimental pilot machines reach up to 58%. Factors determining such dryness are: time of pressing, pressure in pressing zone, construction and quality of felt, as well as temperature and composition of paper tape.

The quantity of water removed from paper in pressing zone is calculated by the equation:

$$dQ = k \bullet \Delta p \bullet dt/\eta \bullet L,$$

Speed of drainage in pressure zone is defined by D'Arcy law:

$$V = dQ / dt = k \bullet \Delta p \bullet 1/\eta \bullet L, \text{ where:}$$

$\Delta p$ – difference of hydrodynamic pressures,
$L$ – thickness of tape,
$\eta$ – viscosity of water,
$k$ – resistance of water stream through tape,
$t$ – pressing time,
$k/L$ is constant, regardless of speed and amount of drained water.

Pressing time, t, depends on width of pressing zone, 2b, and speed of paper machine, V: $t = 2b/V$.

Width of pressing zone (20-350 mm) depends on diameter of rollers and shape of pressure zone (pedals), and is calculated by the equation:

$2b = \Delta h - 2Re$, where $Re = R1 \bullet R2/(R1+R2)$.

Figure 10 shows dependence of pressing zone, 2b, from total compressibility, Δh, that is, from diameter of pressure rollers, Rl i R2. Figure 11 shows expansion of pressing zone depending on compressibility of pressing, that is, from number of felts in pressing zone.

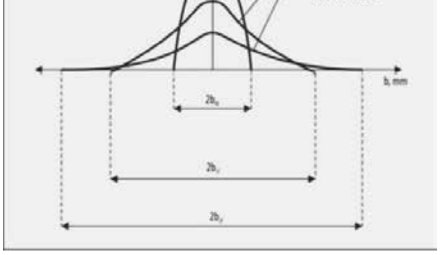


*Fig.11 Dependence of pressing zone from number of felts*

This knowledge gave the idea to researchers to pursue expansion of pressing zone beyond classic pressing rollers. Back in 1980 presses with pressing rollers 1600 mm in diameter have been developed, with pressing zone extended from 25 mm to 65 mm, and soon after that presses with press pedal were developed with pressing zone of full 250 mm.

Figure 12 shows three types of presses: classic, with R= 1.100mm and pressing zone 2b = 25 mm; presses with big roll R = 1600 mm and 2b = 65 mm; and presses with pedal and 2b = 250 mm.

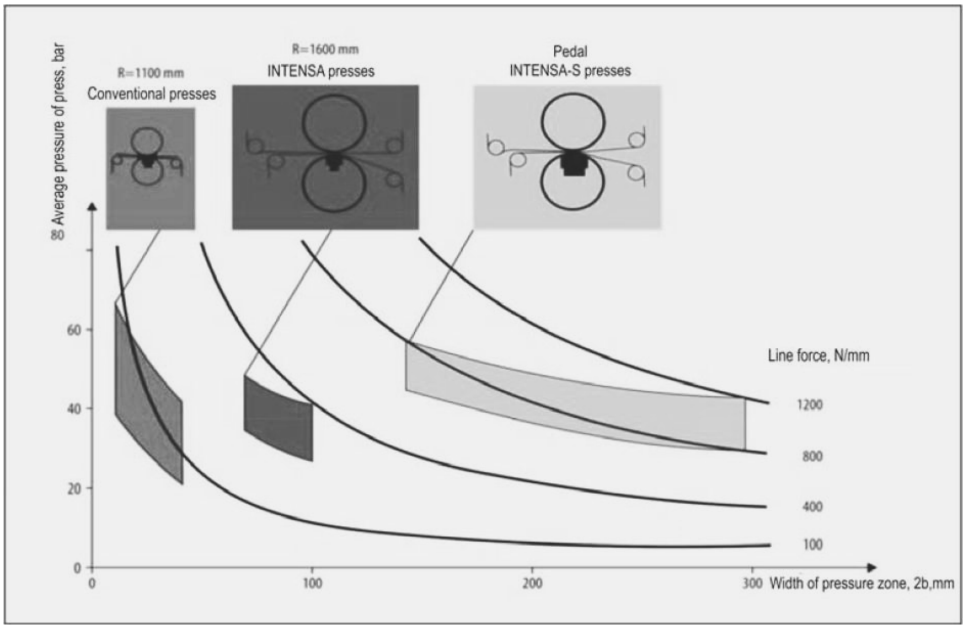


*Fig.12 Three types of presses and three pressing zones*

## 2.2. EXPERIMENTAL PART – PRESSES ON MODEL FHB

This part shows the effects of the reconstruction of press part in Paper Factory Belgrade (FHB) performed during April-May 2012.

Goal of the reconstruction of presses was to:

- increase paper dryness after presses from 41,5 % to 46%,
- decrease consumption of heat energy for approx. 20%,
- increase capacity for approx. 20%,
- automatic leading of paper tape, from sieve through presses and drying part – thus increasing production for additional 3% and releasing burden on staff.
- increase paper quality by enhancing its mechanical properties and visual appearance.

In order to achieve these goals, existing condition of press part has been analyzed (Figure 13), and the starting point was to reach desired goal with minimal investment.

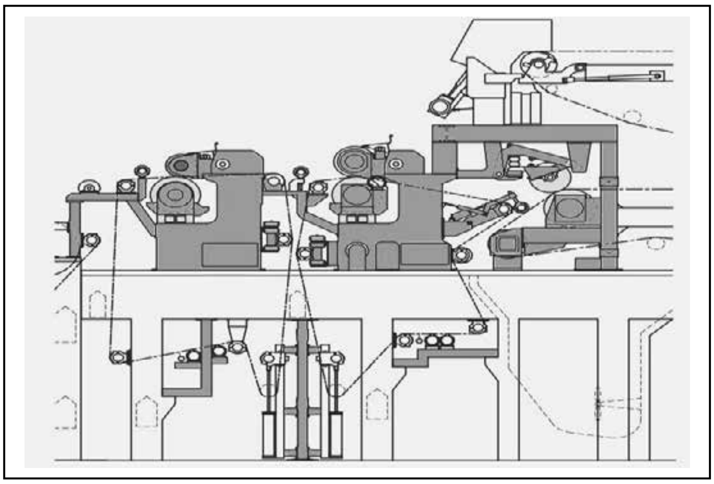


*Fig. 13 Press part in FHB prior to reconstruction*

Also, it was taken into account that Cardboard factory UMKA possessed second hand press rollers, and in combination with existing presses and purchased JAMBO rollers, with diameter 1.200 mm, such a solution can be designed which will comply with requirements (both factories have the same owner). After detailed analysis and design of numerous variants of press part, the solution has been found, as shown in Figure 14.

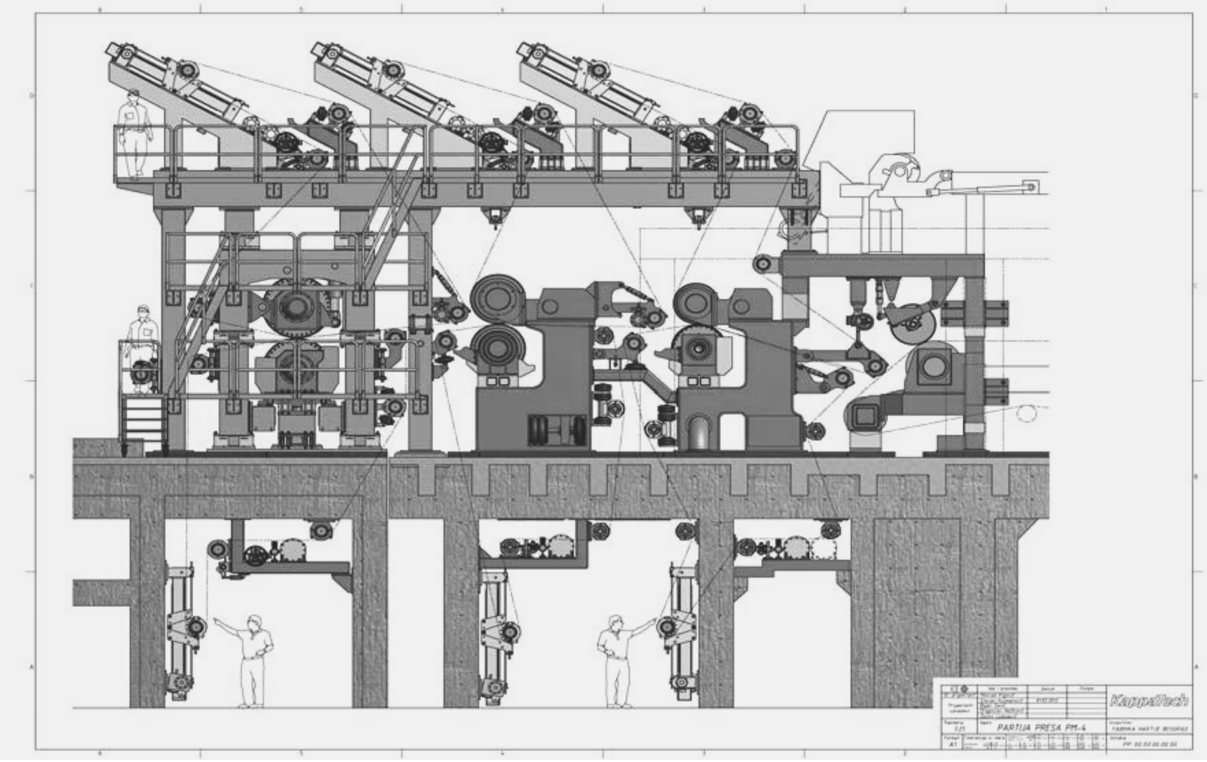


*Fig.14 Press part in FHB after reconstruction*

As seen in Figure 13, press part prior to reconstruction had two NIP with line pressure: for I choke press 40kN/m, and for II "blind punctured" press (drill press) 100 kN/m. These presses had only bottom felts, and paper tape moved freely through presses.

Presses were designed with closed leading of paper tape through press part, and double felts at each press. All rollers were "blind punctured", with precisely determined perforation, except bottom choke roller of the I press. Calculation for newly designed presses was complex and complicated, especially estimation of bulging of rollers which depends on many factors.
Since technically accurate parameters for second hand rollers were hard to find (lack of documentation), the calculation became even more complex, making the result of practically correct line pressure even harder to reach.
This design of the closed system of paper tape leading and automatic vacuum take over of the tape between presses by the transfer choker represents the original solution of Designers.

The innovative solution 3NIP – 2F (3 NIP, with double felts) led to the optimal design of presses with 3 NIP, specifically: I press with line pressure of 65 kN/m, II press with 100 kN/m and III press – JAMBO, with 180 kN/m.

Calculation of the engine power for press drive and adjustment of the installed engine power is also the original solution of Designers.

### 2.3. RESULTS AFTER RECONSTRUCTION OF PRESS PART IN FHB

Bulging of rollers and print on IC diagram:
After installation of presses, IC test or more precisely, the control of the print on rollers was conducted for each press on indigo paper with the projected working line pressure (Figure 15). It can be seen that presses II and III have ideal print, while press I demonstrates weaker bulging. Reason for that is because bottom roller of the I press, with diameter of 3 mm is less bulged than defined in Project. The correction must be performed according to Project in order to achieve desired print.

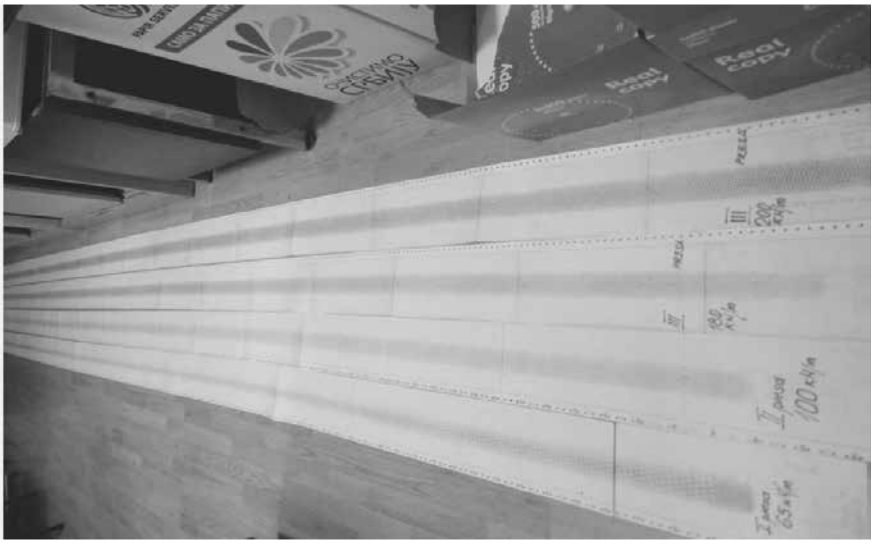


*Fig. 15 IC print – checking of bulging of all three presses*

Paper dryness after press part:

Examination conducted by the FHB Laboratory determined that the dryness of paper after press part is 47%, eight (8) days after production start, at the speed of 230 m/min and the weight of fluting paper of 120 g/m2. Given that produced quantity is 200 t/day, calculated capacity for the full width of PM at the annual level would be 75.500 t/year (Project put the estimation at 75.000 t/year).

Dryness has been increased from 41,5% (reached at the PM speed of 150m/min for fluting weight 120g/m2) to 47,05% (at the PM speed of 233m/min for the same paper weight). According to draining theory in paper pressing zone, dryness of paper tape is strictly depending on the time of retaining in pressing zone, thus giving stronger effect – greater percentage of dryness then figures show, although the increase is 5,55% which enables saving 28% of heat energy. After one year of operation of PM 4 in FHB, **achieved dryness after presses is 49%, representing heat energy saving of 37%!**

Paper quality:

Paper quality has also been increased, giving better mechanical properties as well as visual appearance. Precise data regarding mechanical properties will be obtained after long term monitoring and tuning of production. Cross section of paper humidity has been significantly increased, which also reflected on the increase of output wetness of paper for 1,5-2%. Consumption of heat energy and consumption of fibers for paper production are reduced for the same percentage.

Load of electric engine drive of presses:

According to calculation, where particular load distribution for upper and lower rollers in presses was taken into account (for lower rollers already had oversized engines), engine power for upper rollers was determined, thus decreasing needed power at the expense of the engine power of lower rollers.

## 2.4. DISCUSSION OF RESULTS

According to theoretic knowledge, and the choice of system and design of presses, mathematic and hydrodynamic rules have been verified and then applied on model of reconstructed presses in FHB. Received parameters which give better results than those provided in Project, approved the application of modern technology and original solutions.

As seen in theoretic part, there are presses with pedal (SHU), giving dryness after presses of up to 54%, however installation of such presses requires investment of 6-7 Millions EUR. We estimate that the investment for installed presses was approx. 1 Million EUR.

### 2.5. CONCLUSIONS – RECONSTRUCTION OF PRESS PART IN FHB

Reconstruction of press part on PM4 in FHB accomplished following effects:

1. reduced heat energy consumption for approx. 30 – 37%,
2. increased production for approx. 60 %, from 45.000 to 75.000t/year,
3. decreased consumption of raw material (fibers) for 1.5-2%,
4. increased quality of all mechanical properties of paper,
5. investment four times smaller than that for a new equipment,
6. investment returns in less than a year.

All of this achieved with domestic knowledge, domestic equipment, except second hand rollers for presses.

## 3. DRYING PART: RECONSTRUCTION OF STEAM-CONDENSATION SYSTEM IN PAPER FACTORY BEOGRAD AND PAPER FACTORY LEPENKA

### 3.1. BASIC THERMODYNAMIC PHENOMENA IN PAPER DRYING PROCESS

**Transfer of heat energy**

Paper drying presents combination of process of heat and mass transfer. Heat is brought to paper tape from heated drying cylinders, where water evaporates from surface and from the inside of paper tape. This steam, with simultaneous heat transfer, is led to surrounding air. Transfer of heat energy of the steam to surrounding air depends on: temperature of the inside of cylinder, temperature of the outside of cylinder, temperature of the inner side of tape, temperature of the outer side of tape, temperature of the surrounding air, sieve temperature. Transfers of heat and mass are mutually connected and must be observed jointly (Figures 16 and 17).

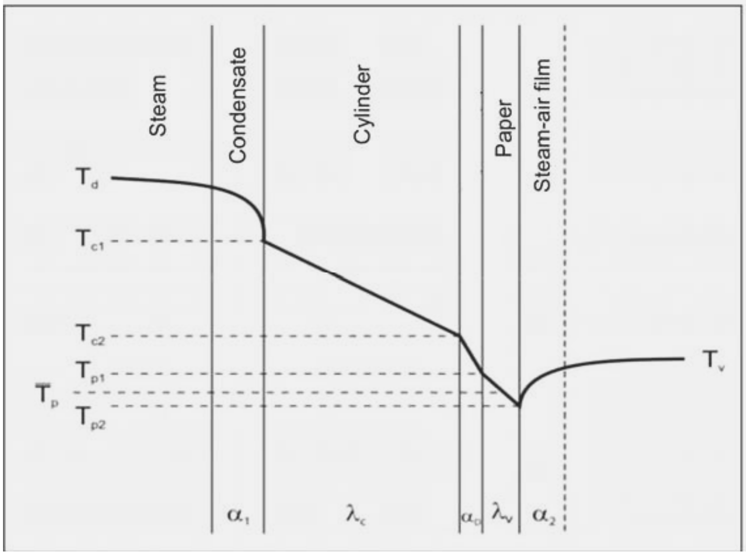


*Fig. 16 Heat transfer*

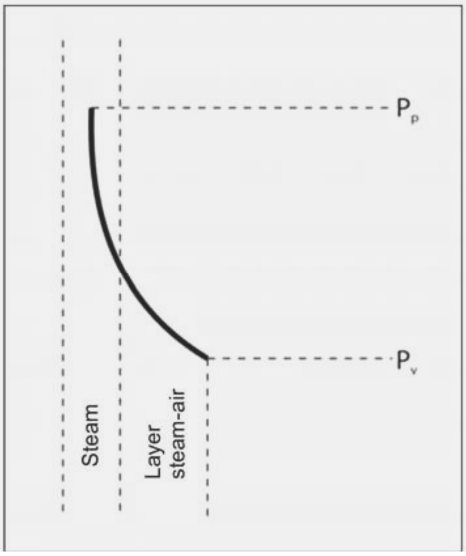


*Fig.17 Mass transfer*

***Heat transfer:***

$Q = [k(Td - Tp) + \alpha\, 2(Tv - Tp)]$, conduction + convection,

$Q = Cp \cdot \Delta Tp$ , cooling – drying, where:

Td – steam temperature,
*Tp* – average temperature of paper tape,
Tv – temperature of air led to paper tape,
α2 – coefficient of transfer steam-air.

***Mass transfer:***

$$mH_2O = \beta\, (Pp - Pv) / R\, T ,$$

where:

β – coefficient of mass transfer,
Pp – partial pressure on the paper surface,

R – gas constant,
T – air temperature.

Heat transfer in the process of paper drying occurs in three ways:

1. conduction,
2. convection and

3. radiation.

***Conduction***

Heat conduction law was set by Furrier:

$Q = \frac{F}{d} \lambda * \bullet (T_1 - T_2) \bullet t, (J)$ , where:

***Convection***

Law of heat transfer from fluid to wall and vice versa was set by Newton:

$$Q = \alpha \bullet F(T1 - T2) \bullet t, (J)$$

From this follows that the heat transfer coefficient, α , is:

$\alpha = \frac{Q}{F \bullet (T_1 - T_2) \bullet t}, (\frac{W}{m_2{}^o C})$ , where

1/α – resistance to heat transfer between fluid and cylinder wall, and the flux of heat transfer is:

$\Phi = \alpha \bullet F \bullet (T1 - T2), (W)$

Heat transfer unites heat conduction and heat crossing, because in reality these two processes never occur separately. By using Newton's law, heat transfer can be expressed as:

$Q = k \bullet F \bullet (T1 - T2) \bullet t, (J)$, and coefficient of heat trasnfer, ***k***, is:

$k = \frac{Q}{F \bullet \Delta T \bullet t}, (\frac{W}{m_2{}^o C})$, where 1/k – resistance to heat transfer.

This coefficient can be calculated from the following equation:

$$\frac{1}{k} = \frac{1}{\alpha_1} + \sum_1^n \frac{d}{\lambda} + \frac{1}{\lambda_2}$$

Heat flux is determined by the equation:

$$\Phi = k \bullet F \bullet (T1 - T2), (W).$$

Specific heat flow (density of heat flow) is quantity of heat which flows in unit of time per unit of area:

$$q = \frac{\Phi}{F} = \frac{Q}{F \bullet t} = \frac{\lambda}{d}(T_1 - T_2) = \frac{(T_1 - T_{2)}}{d / \lambda}, (W / m_2 h)$$

F – cylinder area, m 2,
d – cylinder wall thickness, m,
t – time, s,
T1, T2 – temperature of inner and outer side of cylinder, °C.

From this follows that heat conductivity, λ, is:

$\lambda = \frac{Q \bullet d}{F \bullet (T_1 - T_2) \bullet t}, (\frac{W}{m^o C})$ , and heat flow per time unit is the flux, Φ:

$\Phi = \frac{Q}{t} = \frac{F}{d} \lambda \bullet (T_1 - T_2)$ , $(W)$

**Principle of calculating heat and mass transfer**

***Heat quantity*** transferred by air streaming to the surface of paper, per unit of area, is calculated by the equation:

$$Q = \alpha \bullet (Tv - Tp)\ W/m_2),$$

where:
Q – quantity of heat per unit of area, W/m2
Tv – temperature of hot air brought to paper, oC
α – coefficient of heat transfer from hot air to paper surface, W/m$^2$ $^0$C
Tp – temperature of the paper surface, $^0$C.

***Quantity of mass*** (evaporated water) removed from the paper surface, can be calculated by the following equation:

$$g = \frac{\beta}{R_p \bullet Tm}(Pp - P\upsilon),$$

where:
g – quantity of removed evaporated water from paper per time unit, kg/ m2,s
Rp – gas constant for water steam, J/kg oC
Tm – average absolute temperature of border layer, °C
Pp – partial pressure of water steam on paper surface, kg/m$^2$
Pv – partial pressure of water steam in turbulent core of drying air, kg/m$^2$
β – coefficient of mass transfer (water steam) from paper surface through laminate border layer into turbulent core of drying air, m/s.

Furrier's law is analogue to Ohm's law: I = E/R, where quantity of heat (Q) corresponds to power of current (I), difference (T1 - T2 ) corresponds to difference of potentials E, and heat resistance (d/λ) corresponds to Ohm resistance (R). In order to evaporate quantity of water G from paper, quantity of heat Q must be brought through steam.

$$Q = Qcil. + Qu, \text{ ili } Q = G \bullet r,$$

where:
Q cil. – quantity of heat per one cylinder, which transfers from cylinder to paper, W;
Qu – quantity of heat per unit of time which transfers from surrounding to paper, W;
G – quantity of evaporated water per unit of time, kg/h.
r – heat of water evaporation, J/kg.

These equations represent process of heat energy transfer during paper drying, and the process is shown in
Figure 18.

Quantity of heat brought to paper tape can be expressed as:

$$Q = F \bullet k\,(To - Tpa) + F \bullet \alpha\,3 \bullet (Tu - Tpa), \quad (W),$$

where:
k – coefficient of heat transfer between steam and surroundings, W/m2°C,
To – temperature of hot steam, °C,
Tpa – temperature of the paper tape surface, °C,
α 3 – coefficient of heat transfer between paper and surroundings, W/m2°C,
Tu – temperature of surroundings, °C,
F – drying surface, m2.

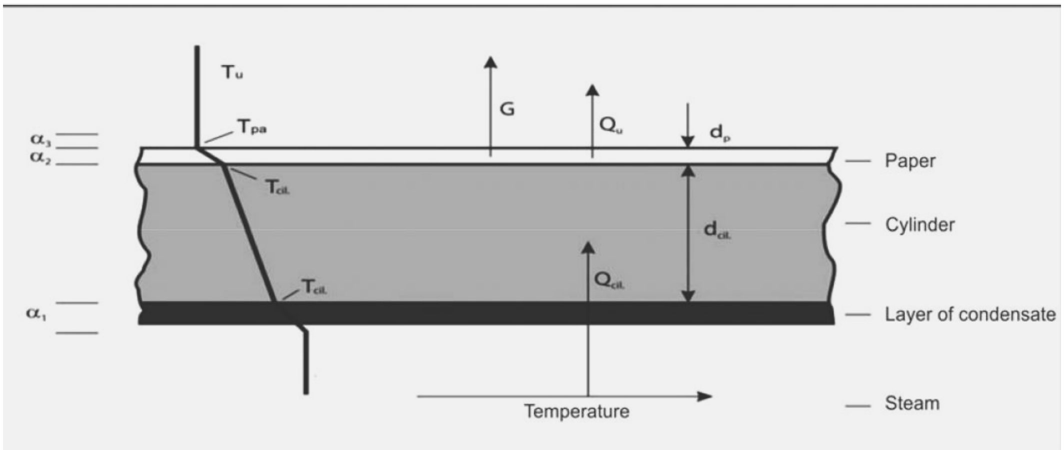


*Fig. 18 Heat and mass transfer during constant drying*

Coefficient of heat transfer, k, is obtained by the equation:

$$\frac{1}{k} = \frac{1}{\alpha_1} + \frac{1}{\lambda_{cil.}} + \frac{1}{\alpha_2} + \frac{d_p}{\lambda_p}, \text{ where:}$$

α1 – coefficient of heat transfer from the inner side of cylinder to the cylinder walls;
dcil. – thickness of the cylinder cover;
λ cil. – coefficient of heat conductivity of the cylinder cover;
α2 – coefficient of heat transfer fro the cylinder surface to paper;
dp. – paper thickness;

Quantity of evaporated water per hour can be calculated by the equation:

$$G = \frac{F}{r} k(T_p - T_{pa}) + \lambda_3 (T_u - T_{pa})$$

Value of the temperature drop between inner side of cylinder and outer side of paper tape is influenced by a number of factors, as shown in Figures 16 and 17.

**Paper drying process**

Water contained in paper at the time of its arrival to drying cylinders, consists of free and chemically bound water. Free water is present on the surface of fibers and in capillaries. It evaporates relatively easy. Bound water presents 23-37% of total weight of paper tape and is stiffened – bound in fiber cells. Its evaporation demands significantly greater energy.

During primary period of paper drying free water evaporates. Speed of drying in this period is determined by the intensity of water evaporation from paper surface and does not depend from speed of diffusion within paper. Temperature of paper in this period is constant, and the air moisture around paper is close to the dew point. This period includes 50-60% of total drying process, and the speed of water evaporation during that period is:

wo = ki (PS-PD) •760/H, ( kg H2O/m2), where:

ki = 0,0229+0,0174v, (kg H2O/m2 , s, kPa) coefficient of the evaporation speed;

Ps – partial pressure of water steam at the evaporation temperature, kPa;

PD – partial pressure of water steam in surrounding air, kPa;

H – barometric pressure of surrounding air, kPa.

With increased temperature of paper, speed of water evaporation also increases. During decreasing partial pressure of water steam in surrounding air, achieved by proper ventilation, the speed of evaporation rises.

Evaporation also increases by decreased barometric pressure H (drying in vacuum). Former equation gives basic factors which influence on speed of water evaporation in first part of drying part. Primary drying period lasts until paper dryness of 65-70%.

In secondary drying period, where evaporation of hygroscopic bound water starts, the intensity of evaporation slowly decreases and the temperature of paper rises.

Speed of drying in this period depends on the speed of diffusion of water in paper and gradually decreases with decreasing of paper humidity. Speed of diffusion depends on paper humidity, type of fibers, rate of granulation, paper thickness etc. Speed of drying in secondary period also depends on contact between paper and cylinder, type of drying sieves, their tension, ventilation etc. Therefore, process of paper drying on drying rollers can be divided into three zones – phases of evaporation of water from paper (Figure 19).

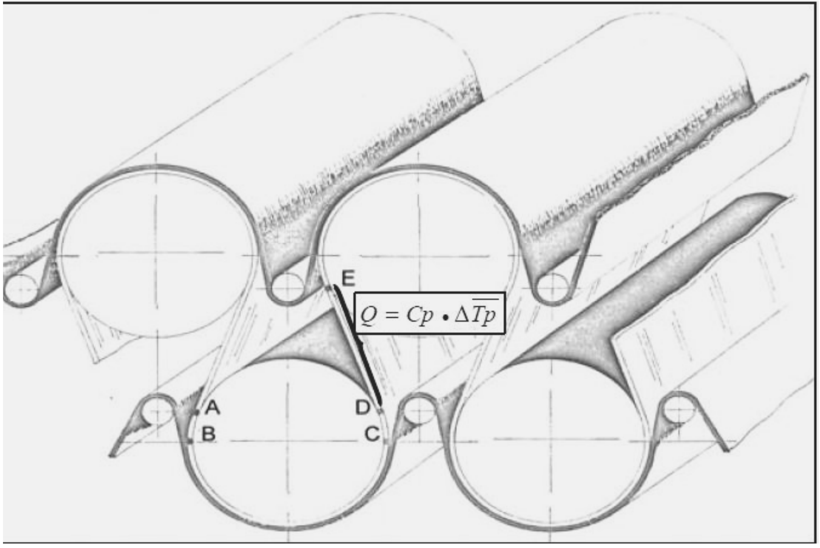


*Fig. 19. Phases of paper drying on drying cylinder*

Part A-B and opposite, symmetrical part, C-D, art not covered by drying sieve. At these parts paper is in contact with cylinder, but since there is no sieve pressure, contact between them is weak. Therefore evaporation on these parts is lesser and does not go beyond 5-10% of total quantity of evaporated water.

Paper on part B-C is pressed by sieve to the cylinder. In this section main water evaporation occurs (80-85% on slow-running and 60-75% on speed-running paper machines).

Speed of water evaporation on part B-C is greater than on part A-B due to better contact between paper and cylinder, and also because the difference between partial pressures of water steam evaporated from paper and water steam in the structure of drying sieves is greater than the difference of partial pressures of water steam evaporated from paper and water steam in surrounding air.

Tertiary period of drying includes interval D-E, where paper moves freely between cylinders. Unlike first two drying periods, where heat is brought to paper, water evaporation in tertiary period is the consequence of heat accumulation during first two drying periods. Paper tape in tertiary drying period is cooled by 4-5°C on fast and 12-15°C on slow paper machines. Previously stated formula for heat transfer $Q = Cp \cdot \Delta Tp$ , is valid for this part, for the phase cooling-drying of paper, part D-E, Figure 19. With the increase of machine speed, the quantity of water evaporated in third phase rises and can reach 20-30% of totally evaporated water.

It can be explained by smaller drop of temperature of tape on this part at fast machines, creating smaller border layer of saturated air on the paper surface. This manifestation explains smaller intensity of water evaporation from paper on multicylinder machines in relation to single-cylinder, where heat transfer is continual during whole drying process.

Intensity of drying is determined by following factors:

- temperature and pressure of steam in cylinders;
- ventilation of drying part;
- type of drying sieves and size of contact between paper and cylinder, depending on tension of sieve;
- diameter of drying cylinders and distance between their centers, horizontally and vertically, of which depends length of free part of paper tape, Figure 19, part D-E;
- possibility of removing condensation and air from drying cylinders, and purity of their surface (coefficient of heat transfer from steam to paper depends from these factors);
- paper properties (weight, composition, granulation, porosity, filler content, primary-secondary fibers...).

Determination of factors which influence the drying process is very complex and demands detailed examination on every PM, as was the case in FHB and in LEPENKA.

In this part of work we will discuss steam-condensation system, because results received by its reconstruction are reflected in energy saving on paper machine.

$$Q = Cp \cdot \Delta Tp$$

### 3.2. STEAM-CONDENSATION SYSTEM

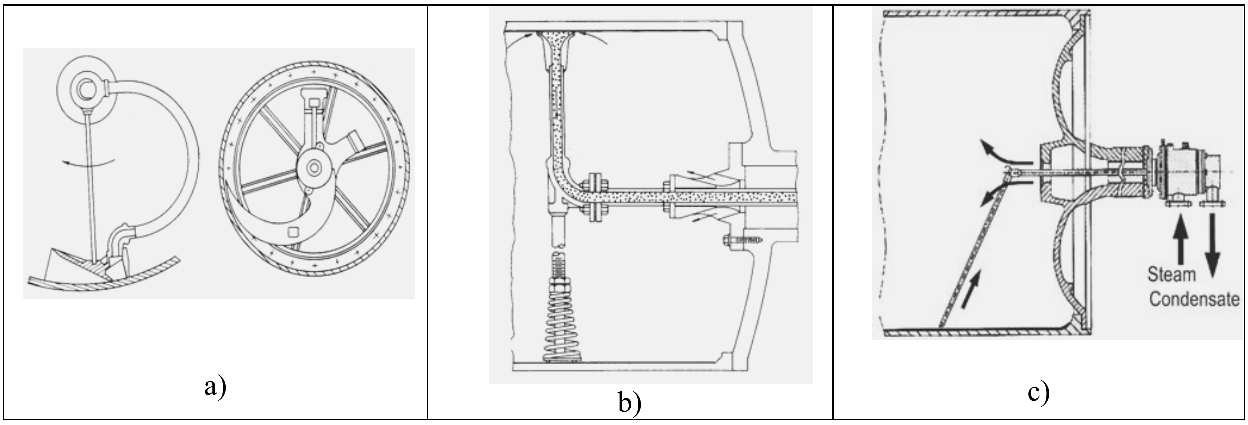
As is known from thermodynamics, one millimeter of condensate of water steam in drying cylinders creates resistance to heat conductivity equal to 27mm of steel and invokes drop of temperature on the surface of cylinder of 4,6%. For that reason, well programmed draining of condensate from drying cylinders enables efficient functioning od drying part, and thus functioning of paper machine with high energy efficiency.

Therefore, devices for draining of condensate from drying cylinders, which influence the condensate draining, must be analyzed.

There are three contemporary systems of siphons for draining condensate from cylinders, namely:

2. spoon, Figure 20a,
3. rotating syphon, Figure 20b, i
4. stationary syphon, Figure 20c.

Spoon system which was until now built into PM4 in Paper factory Belgrade, in ideal conditions had condensate 6 mm thick, which influenced decrease of heat transfer from steam to the surface of cylinder, just as the wall of cylinder would be 150 mm thick.

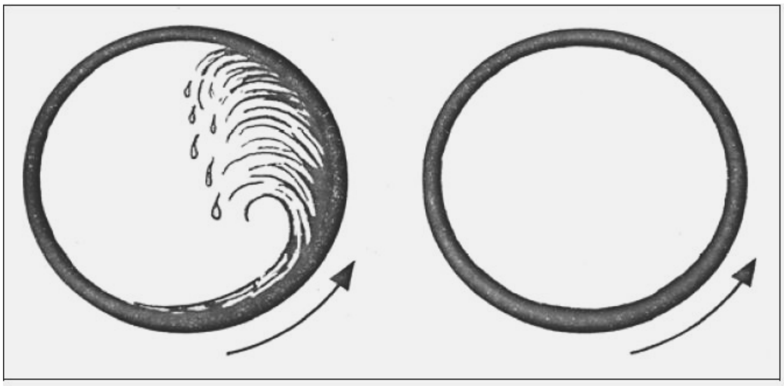


a) b) c)

*Fig.20 Syphon types: a – spoon, b – rotating, c – stationary*

Otherwise, usual thickness of steel cylinder wall in such constructions for the working steam pressure of 5 Bar is 27 mm. Beside great resistance in heat transfer, there is also increased electric power consumption on these cylinders for the drying part drive, due to accumulated condensate in cylinders.

During creating larger amount of condensate in cylinders, the load of engine for cylinders drive rises, and condensate appearing in cylinders at lower speeds does not form ring but collapses and creates impacts on the bottom of cylinder. Therefore oscillations in load of engine occur, and thus oscillations in speed of drying group. For that reason, continuous production of paper is impossible because paper tape breaks between groups, as a consequence of impossible synchronization of speeds and differences in speed between drying groups. Figure 21 shows cylinder with larger quantity of condensate, where water impacts and oscillation of speed of drying rollers occur. When speed of cylinders rises, condensate turns into ring and the speed of cylinder stabilizes, and the engine load gradually decreases and then suddenly rises.



a) b)

*Fig.21 Condensate in cylinder: (a) low speed – condensate, (b) great speed – ring of condensate*

Figure 22 shows load of engine depending on speed of paper machine and condition of condensate in cylinder: condensate or ring of condensate.

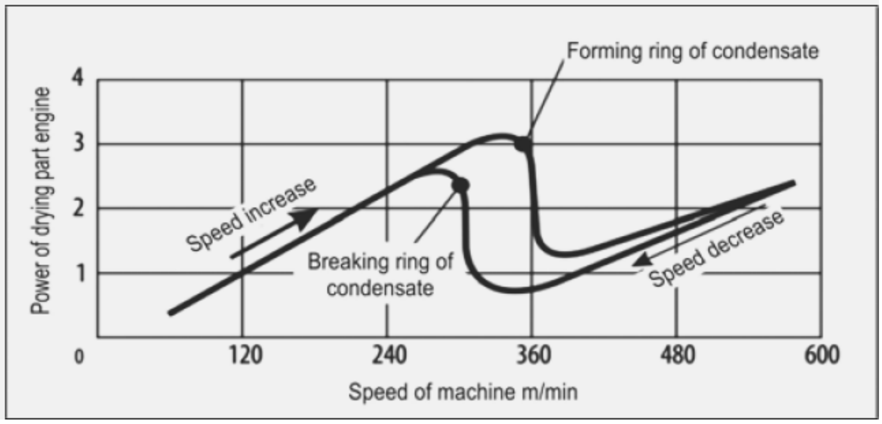


*Fig. 22. Dependence of engine load from the speed of machine and condition of condensate in cylinder*

Diagram in Figure 22 shows that critical point of engine load, which causes turn of the condensate into ring of condensate, is ate the 360 m/min, after which ring is created and it causes sudden decrease of engine load.

Further increase of the speed of paper machine, engine load gradually rises, proportionally to the increase of speed of PM.

If we decrease speed of paper machine, engine load will drop until speed of 300 m/min, when lower critical point, so-called hysteresis, appears. At that point ring turns into condensate, engine load suddenly rises and speed of paper machine becomes unsynchronized (such was the case in FHB on PM4 on May 21st 2010)

Installation of modern siphons into drying cylinders of PM for draining condensate from cylinder (rotating, Figure 20b or stationary, Figure 20C), in normal working conditions, gives thickness of condensate ring of 1.6 mm. Although both these systems are modern, with high level of condensate draining, there are differences in energy efficiency between them.

### 3.3. REALISATION OF THE RECONSTRUCTION PROJECT OF STEAMCONDENSATION SYSTEM ON PM4 IN PAPER FACTORY BELGRADE

By detailed studying theory and practical experiences, as well as comparative analysis of pros and cons of rotary and stationary siphons, as well as cascade and thermo compression systems, we have decided to choose: **stationary siphons and combined cascade-thermo compression steam-condensation system**.

Diagram of SCS after reconstruction of PM4 is shown in Figure 23. System was designed with high level of heat utilization, all of steam has been utilized, i.e. there is no heat loss. The accuracy of this is confirmed by the fact that the annually 75.000 tons of packaging paper is being produced in drying group of 28 drying cylinders with Yankee cylinder and Lime press for chemical coating.

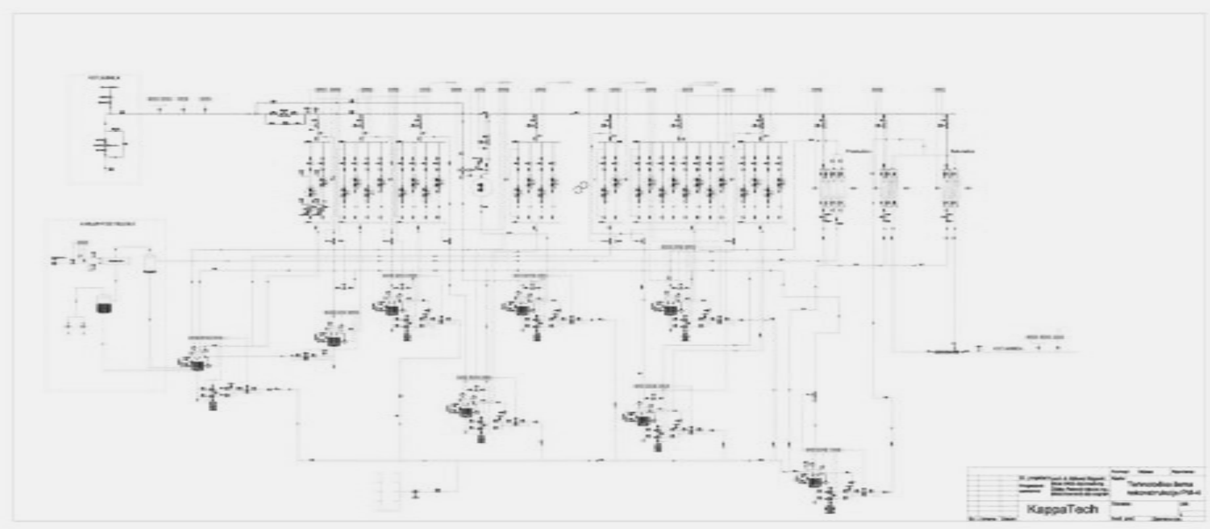


*Fig. 23 Cascade thermo-compression SCS after reconstruction of PM*

### 3.4. RECONSTRUCTION OF STEAM-CONDENSATION SYSTEM ON PM1, LEPENKA, NOVI KNEZEVAC

Since there was separate reconstruction of SCS on this machine, detailed monitoring of the condition of technology before and after reconstruction have been conducted. Mathematical approach to the evaluation of the effects of reconstruction of SCS in Lepenka has been applied according to TAPPI standard. First step was to record all relevant factors on PM which influence the drying process. Specific consumption of heat and electric energy in drying part was recorded in dynamic and stable technological and production conditions. Recording was performed before reconstructions, and under same conditions, after reconstruction of SCS.

#### Condition prior to reconstruction

Recording of the existing condition od technical parameters on PM1, which presented basis fro project of reconstruction of SCS, has been executed according to unique check list, according to which measurements were made. The production on PM1 for 2011 and first quarter of 2012 is given by the sorts of paper, monthly, measured on roller, for fluting, srenc and test liner, gross values. In production of these paper sorts, during continuous production and at full working width, a speed of PM has been measured and all relevant data for paper production in pulp preparation, sieve part, press part, drying part and roller was demanded.

Also, a number of changes of air in hall per hour had to be measured and the existing documentation of SCS had to be provided, and thermic parameters on SCS as well as rate of condensate return to boiler had to be recorded.

Figure 24 shows actual condition in drying cylinders and draining of condensate prior to reconstruction.

Drying cylinders were half filled with condensate, i.e. up to the level of cylinder branch, through which the pipe for condensate draining passes. This phenomenon was caused by thermostats built on pipelines for condensate draining, and they were installed on all drying cylinders (Figure 25).

In order for PM to achieve speed of 195 m/min for 127g/m2 fluting, a pressure of steam in main steam line was 3 bar, in I drying group it was 2.6 bar, in II drying group was 1.3 bar and in III drying group 0.28 bar.

Specific consumption of steam for production of srenc paper was 2.48 t of steam/t, and for fluting 3,0t/t of paper. Average engine load in drying groups was 50.7 A.

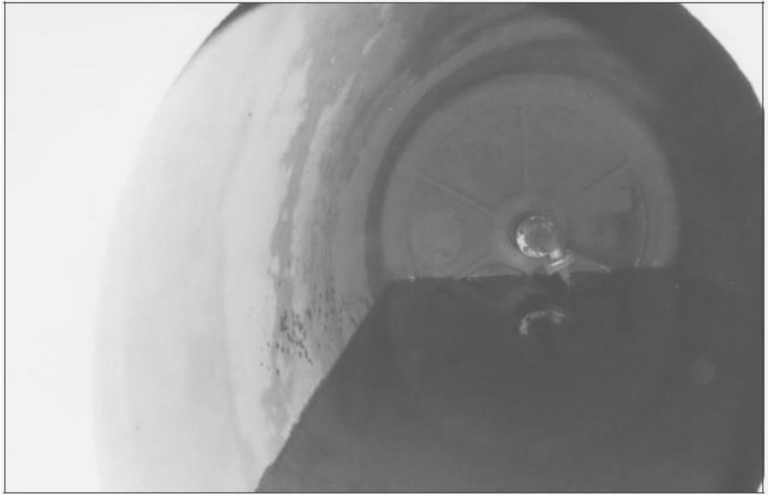


*Fig. 24. Inner appearance of cylinder, with condensate*

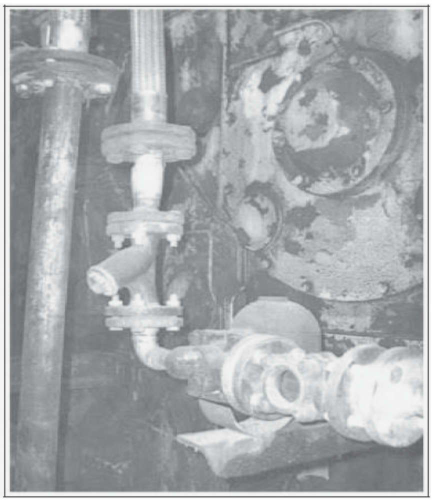


*Fig. 25. Built thermostats on pipelines for condensate draining*

**Condition after reconstruction**

SCS has been reconstructed as a cascade system with three thermic groups, as shown in Figure 26. Optimal SCS with high thermic efficiency was designed with four thermic drying groups and heat exchangers where so-called Brid steam was used for heating fresh air. However, due to lack of investment means, construction of this system has been postponed for the next phase of reconstruction. Existing stationary siphons for condensate draining were utilized, with correction of „heads“, in order to achieve desired distance of 3mm between cylinder and syphon.

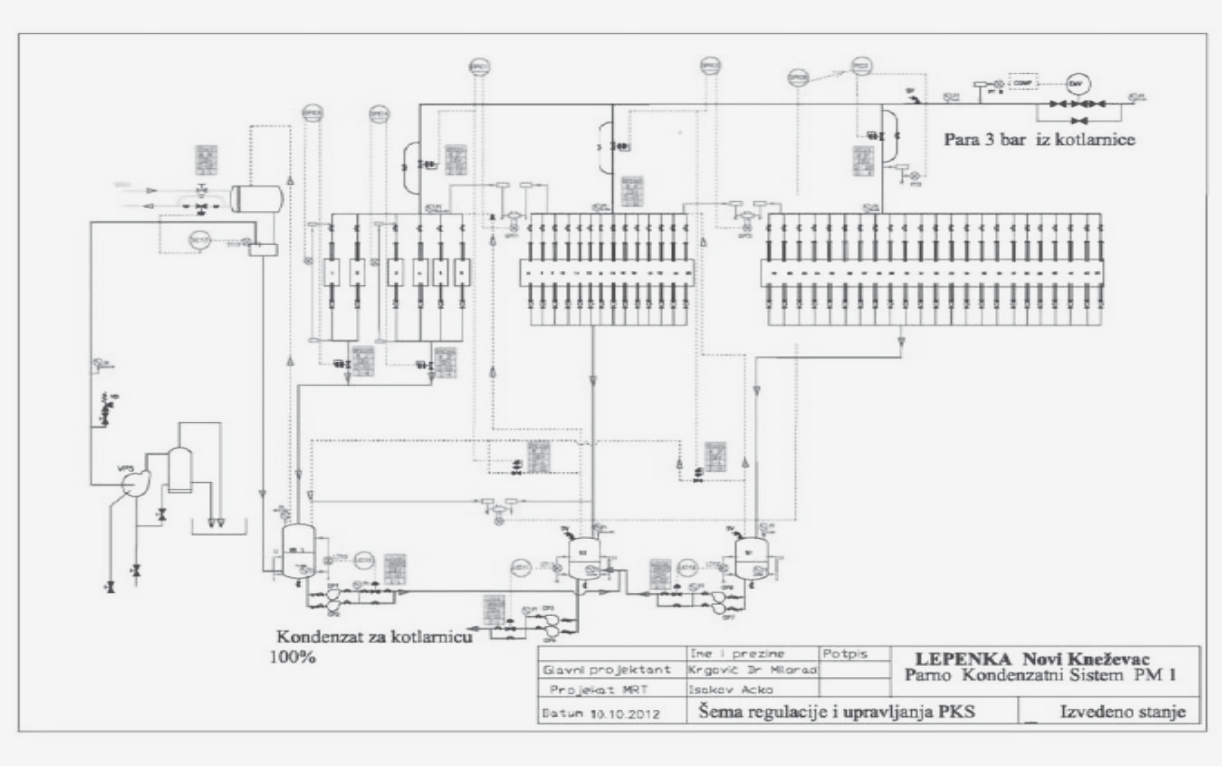


*Fig. 26 SCS in LEPENKA after performed reconstruction of PM1*

Whole system of steam pipelines has been reconstructed, as well as system for condensate draining and vacuum facility. Measuring and regulation devices were built for the automatic regulation of whole SCS, with optional attachment to computerized automatic management and regulation of paper humidity.

After reconstruction and test and commercial production, whole system has been examined under same methodology as prior to reconstruction.

All drying cylinders were checked and it was noted that they were empty – there was no retained condensate in them, as shown in Figure 27. Figure 28 shows steam supply and condensate draining from cylinders, where it can be seen that there are no thermostats on pipelines for condensate draining, since such thermostats are not anymore applied in modern SCS. Recorded results of the examination after reconstruction of SCS are shown in table 1 and 2, and table 3 shows results six months after reconstruction.

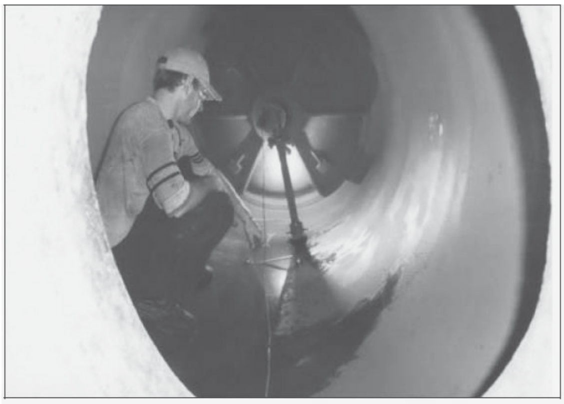


*Fig. 27 Interior of cylinder without condensate, after reconstruction*

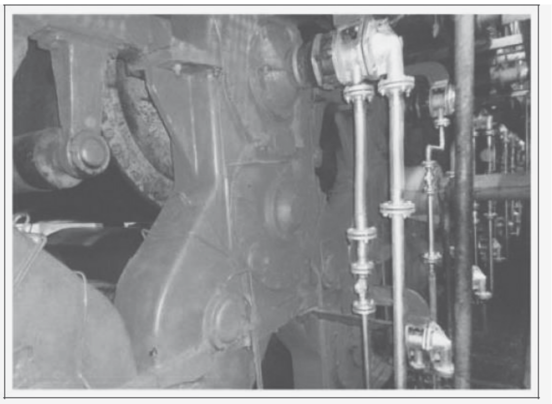


*Fig.28 Steam supply and condensate draining without thermostats*

*Table 1 Conducted measurements and period of verification of guaranties according to TAPPI standard – srenc*

| ***31.10.2012.*** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ***Time of measurement*** | ***Sort of paper, weight, g/m2*** | ***Paper production, t/h*** | ***Steam consumption, t/t*** | | ***Steam-heat energy saving, %*** | ***Electric power consumption, A*** | | ***Electric. energy saving, %*** |
| | | | *Before* | *After* | | *Before* | *After* | |
| *12.15h* | *Srenc, 180* | *5,025* | *2,48* | *2,0* | *19,4* | *50,7* | *27,0* | *46,7* |
| *12.45h* | *Srenc, 180* | *4,95* | *2,48* | *1,98* | *21,0* | *50,7* | *27,5* | *46,6* |
| *19.00h* | *Srenc, 100* | *3,36* | *2,48* | *1,88* | *24,0* | *50,7* | *29,9* | *42,0* |
| *20.10h* | *Srenc, 100* | *3,39* | *2,48* | *1,80* | *27,4* | *50,7* | *29,8* | *42,0* |
| ***average*** | | | ***2,24*** | ***1,99*** | ***19,76*** | ***50,7*** | ***28,85*** | ***43,0*** |
| ***01.11.2012.*** | | | | | | | | |
| *10.00h* | *Fluting, 127* | *4,47* | *3,0* | *2,41* | *19,67* | *50,7* | *31,7* | *38,7* |

*Table 2 Measured parameters on PM on 21. i 22. November 2012 – fluting*

| ***Time*** | ***P3*** | ***DP2*** | ***DP1*** | ***Vac.I*** | ***T17*** | ***Pul*** | ***Load of drying groups, A*** | | | | | | ***S1*** | ***S2*** | ***V PM*** | ***Q.st.*** | ***Weig.*** | ***Width*** | ***SPP*** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *bar* | *bar* | *bar* | *bar* | *oC* | *bar* | ***I*** | ***II*** | ***III*** | ***IV*** | ***V*** | ***VI*** | *bar* | *bar* | *m/min* | *m3/h* | *g/m2* | *cm* | *t/t* |
| | | | | *-0.30* | *85* | *3* | ***30*** | ***30*** | ***20*** | ***25*** | ***25*** | ***38*** | *1,8* | *1* | *232* | *9,8* | *127* | *220* | *2,51* |
| *10:50* | *2,89* | *0,78* | *0,96* | *-0.30* | *85* | *3* | *35* | *29* | *20* | *25* | *24* | *33* | *2,2* | *1,5* | *182* | *11,5* | *180* | *217* | *2,69* |
| *11:50* | *2,77* | *0,78* | *0,92* | *-0.27* | *90* | *2,8* | *35* | *30* | *20* | *25* | *23* | *34* | *1,8* | *1,2* | *182* | *11,3* | *180* | *217* | *2,65* |
| *12:50* | *2,46* | *0,75* | *0,83* | *-0.28* | *85* | *3,7* | *33* | *29* | *20* | *24* | *29* | *29* | *1,6* | *0,8* | *182* | *12* | *180* | *217* | *2,81* |
| *14:55* | *1,72* | *0,43* | *0,45* | *-0.28* | *76* | *1,8* | *33* | *27* | *23* | *24* | *28* | *36* | *1,6* | *0,6* | *236* | *9,5* | *127* | *215* | *2,45* |
| *19:00* | *1,65* | *0,53* | *0,52* | *-0.32* | *80* | *1,7* | *37* | *30* | *24* | *26* | *31* | *41* | *0,8* | *0,4* | *236* | *8,1* | *127* | *215* | *2,09* |
| *20:00* | *1,7* | *0,53* | *0,52* | *-0.30* | *80* | *1,7* | *38* | *31* | *23* | *25* | *32* | *40* | *0,8* | *0,4* | *236* | *10,2* | *127* | *215* | *2,64* |
| ***22.11.2012, measuring steam flow, fluting 127/215 , speed 236 m/min*** | | | | | | | | | | | | | | | | | | | |
| *11:50* | | | | | | | | | | | | | | | *236* | *9,6* | *127* | *215* | *2,48* |
| *12:50* | | | | | | | | | | | | | | | *236* | *9,5* | *127* | *215* | *2,45* |

*Table 3 Measured parameters on PM on 29.03.13., speed of PM 195m/min, srenc 110/220g/m$^2$*

| ***P3*** | ***DP2*** | ***DP1*** | ***Temp cond in collector, oC*** | | | ***Load of drying groups, A*** | | | | | | ***Vac. PM*** | ***Weight*** | ***Width*** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *bar* | *bar* | *bar* | ***I*** | ***II*** | ***III*** | ***I*** | ***II*** | ***III*** | ***IV*** | ***V*** | ***VI*** | *(-bar)* | *g/m2* | *cm* |
| *0,95* | *0,35* | *0,20* | *100* | *95* | *75* | *34* | *25* | *35* | *25* | *30* | *25* | *- 0,32* | *110* | *220* |

***Note:*** *P3 – steam pressure in main pipeline, DP2- differential pressure between I and II drying group, DP1 – differential pressure between II and III drying group, Vac.I – vacuum in I drying group, T17 – exit temperature of water on condenser, S1 – pressure in collector I, S2 – pressure in collector II, SPP – specific consumption of steam, Vac. PM – vacuum on PM.*

Table 2 shows that speed of PM is increased from 195 m/min before, to 236 m/min after reconstruction.

Data from table 3, received on the basis of measurement 6 months after reconstruction of SCS at the speed of 195 m/min, same as prior to reconstruction, indicate key factors of the effects of reconstruction.

Steam pressure in main pipeline is 0.95 bar, and prior the reconstruction it was 3.0 bar. Temperature in separator of first thermo group after reconstruction was 100oC, and prior to reconstruction it was 121oC.

There is no loss of heat on vacuum condenser after reconstruction, and the temperature of cooling water is 32°C with minimal consumption of fresh water. Prior to reconstruction this temperature was 75°C, with much greater fresh water consumption. Engine load for drying groups was 29 A, and prior to reconstruction it was 50.7 A.

This data, achieved in real practice on PM LEPENKA, is in direct correlation with thermodynamic procedures in paper drying process, shown in Figures 29 and 30.

Figure 29 shows that with increasing thickness of condensate from od 0 to 10mm in drying cylinder, coefficient of heat transfer changes from 1.000 to 4.000W/m$^2$ °C.

Figure 30 show influence of thickness of condensate in cylinder, from 2 to 14 mm, under various speeds of PM, on needed engine power, per meter of width of paper machine.

Also, there were examinations of the influence of condensate in drying cylinders on the number of malfunctions of PM before and after reconstruction, Figures 31 and 32.

Diagram 31 shows that 78% of total number of more important malfunctions of PM accounts for synchronization of drying groups speed.

Diagram 32 shows that after reconstruction there is no malfunctions due to synchronization of drying groups speed.

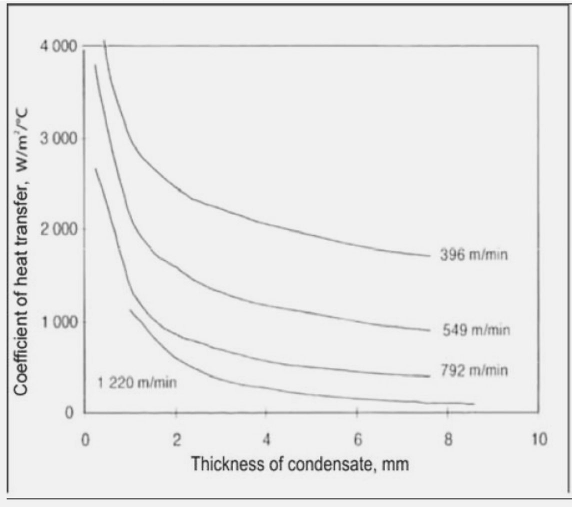


*Fig. 29 Coefficient of heat transfer, as function of the speed of drying cylinder and condensate thickness*

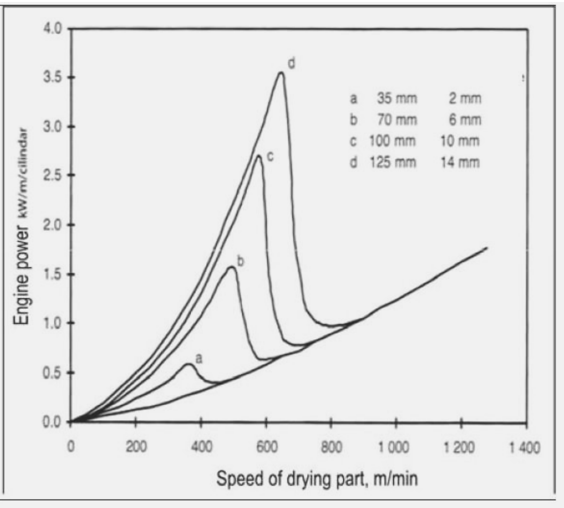


*Fig. 30 Engine power needed to drive drying cylinder with diameter 1500 mm for various thickness of condensate in cylinder*

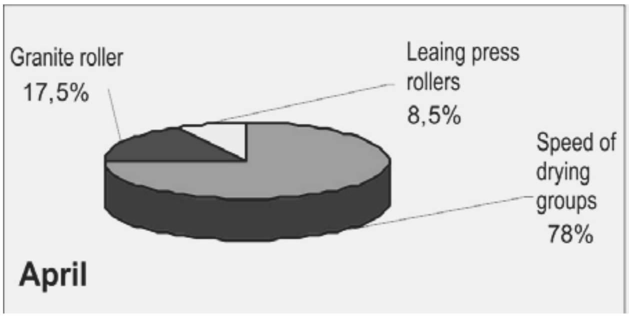


*Fig.31 Malfunctions of PM prior to reconstruction*

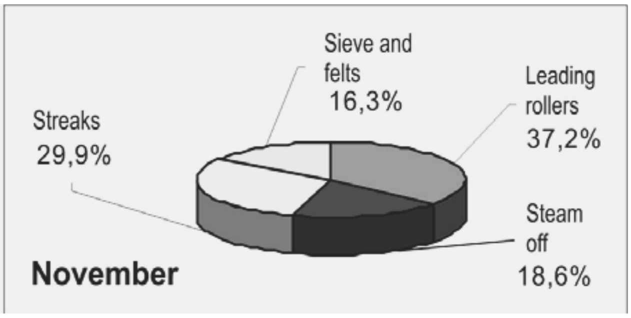


*Fig. 32 Malfunctions of PM after reconstruction*

## 3.5. DISCUSSION OF THE RESULTS

Based on conducted measurements and received results shown in tables 1, 2 and 3 and in diagrams shown in Figures 12 and 13, the effects of the reconstruction of SCS on PM LEPENKA are as follows:

***Heat energy:***

1. specific steam consumption has been decreased from 2,48 t/t to1,99 t/t for srenc paper. In that way steam consumption has been decreased for 0,49 t/t, or 19,75%;
2. specific steam consumption in fluting production (from semi pulp made of straw and waste paper) has been decreased from 3,0t/t to 2,40t/t of paper. Thus there was a saving of 0,59t steam/t fluting (19,67%);
3. after comparing these results with thermodynamic laws of heat transfer, Figure 29., the conclusion is that the results could have been expected, i.e. provided by project;
4. decrease of steam pressure in main steamline from 3,0 bar, prior to reconstruction, to 0,95 bar after the reconstruction, and temperature of condensate in first separator from 121 to 100ºC, at the same speed of PM of 195m/min, also is in correlation with theoretic assumptions, Figure 33. This enabled increase of thermic capacity of drying part, and therefore speed of PM, from 195 to 235m/min, representing increase of 20,5%.

***Electric energy:***

1. reconstruction of SCS decreased load of engines in drying groups from 50,7A to 29,85A, which is decrease of 43%. These results are in correlation with theoretic assumptions shown in Figure 30. Calculations given in concept and master project provided saving 46% of electric energy, with given guaranties of 8%.

*After summing up achieved results and predictions in project, the conclusion is that they are within the limits of expected, and also better than given guarantees.*

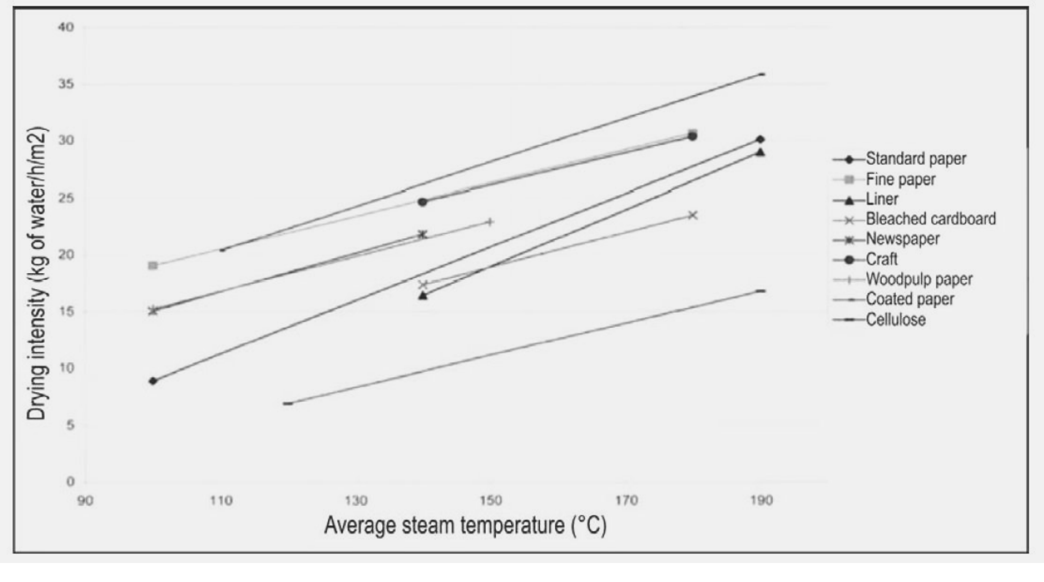


*Fig. 33 Diagram of the intensity of drying for various sorts of paper and cardboard*

## 3.6. CONCLUSION – RECONSTRUCTION OF STEAM-CONDENSATION SYSTEM

**I. SCS on PM4 in Paper factory Belgrade,** previously pressure-flow system with spoon condensate draining from cylinders, has been reconstructed into cascade thermo-compressor system with stationary syphon.

The effects were following:

1. decreased steam consumption for approx. 10 %,
2. decreased electric power consumption for approx. 8%,
3. increased production for approx. 8%,
4. investment decreased 2-3 times in relation to standard,
5. investment returned in approx. 3-4 months.

Everything has been realized with domestic knowledge, equipment providers, installation and commissioning.

**II. The results of the reconstruction of SCS on PM1 in LEPENKA Novi Knezevac**, were following:

1. decreased heat energy consumption for 19,7%;
2. decreased electric power consumption for drying cylinders for 43%;
3. increased speed of PM for 20%;
4. eliminated malfunctions of PM due to unsynchronized drying part and thus increased utilization of working hours of PM.

This model proves that it is possible to theoretically predict practical results of the reconstruction.

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# HÂRTIE CU NANOPARTICULE MAGNETICE

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## Rezumat

Falsificarea documentelor este o activitate infracțională care produce pierderi anuale de miliarde de dolari în intreaga lume. Hârtia securizată este printre cele mai importante elemente utilizate în lupta contra falsificării documentelor publice sau private. Continua diversificare şi creştere în complexitate a tehnicilor de securizare a hârtiei este una din cele mai importante căi de limitare a încercărilor de falsificare. Nanoparticulele magnetice sunt o varianta viabila de securizare a hârtiei. Literatura menționează diverse metode de obținere a hârtiei încărcate cu nanoparticule magnetice. Lucrarea prezintă rezultatele unui studiu referitor la influența nanoparticulelor magnetice asupra proprietăților hârtiei.

**Cuvinte cheie:** Hârtie securizată, Coloizi, Nanoparticule magnetice, Falsificare, Documente de valoare

## Abstract

Document forgery is a criminal activity that causes billion dollar losses each year worldwide. Security paper is among the most important ingredients used in the fight against the forgery of private or public documents. The continuous diversification and sophistication of the paper securing techniques is one of the most important ways to erect fences against forgery attempts. Magnetic nanoparticles are a good candidate for securing elements of security paper. Various methods for the synthesis of paper loaded with magnetic nanoparticles has been reported in the literature.

We present the results of a study concerning the influence of the loading of magnetic nanoparticles on the paper's properties.

**Keywords:** Security paper, Colloids, Magnetic nanoparticles, Forgery, Value documents

# I. INTRODUCERE

Hârtiile destinate tipăririi documentelor de valoare fac parte din categoria hârtiilor speciale. Deşi cantitativ au o pondere redusă în producția mondială de hârtii şi cartoane, acestea au o importanță economică deosebită şi un anumit rol personal şi social bine definit.

Cel mai mare risc la care sunt expuse documentele de valoare îl reprezintă riscul contrafacerii şi falsificării. Se falsifică documentele de valoare fixă (bancnote, cecuri, documente de proprietate etc.), documente cu valoare negociabilă (cecuri bancare, etc.) şi documente sociale personale (acte de identitate, paşapoarte, diplome de studii etc.).

Hârtiile de valoare sunt hârtii de calitate superioară având caracteristici fizico-mecanice - rezistență mecanică ridicată, comportare foarte bună la tipărire (pe aceste hârtii se pot imprima desene de mare finețe, în mai multe culori, pentru evitarea falsificării) şi rezistență deosebită în circulație. În afară de aceste caracteristici hârtia destinată tipării actelor de valoare trebuie să conțină o serie de elemente de securitate care să o facă greu de falsificat.

Pentru ca securitatea documentelor să fie cu un pas înaintea tehnicilor, în evoluție, folosite de către cei care se ocupă de contrafaceri şi falsificări, se impune ca şi sistemul de securizare să fie mereu dinamizat cu noi elemente de securitate, cât mai complexe. Pe de altă parte, fiecare document se realizează pe un anumit sortiment de hârtie securizată, ceea ce înseamnă că tipărirea unui număr mai mare de documente impune automat şi diversificarea grupei de hârtii securizate.

Elementele care pot fi utilizate pentru securizarea hârtiilor pot fi: microparticule (nanoparticule) complexe în următoarele variante:

- Pigmenți organici sau minerali fluorescenți
- Pigmenți sub formă de pulberi magnetice fluorescente sau coloizi magnetici
- Microparticule inteligente de tip MHC – microparticule metalizate holografice codate

Astfel, pigmenții - microparticule de natură minerală sau organică asigură prin compatibilitatea lor şi randamentul de retenție în compoziția hârtiei funcția de element de securizare. Detecția acestor microparticule este dată prin culoarea pe care o prezintă în domeniul vizibil şi de prezentarea fenomenului de fluorescență în prezența radiațiilor UV.

O altă grupă nouă de microparticule, care pot fi introduse în structura hârtiei se referă la pulberile magnetice fluorescente sau coloizi magnetici. Spre deosebire de prima categorie de microparticule, pulberile magnetice fluorescente mai vin în plus cu o proprietate care poate fi ”speculată” în procesul de securizare a hârtiei şi anume – proprietățile magnetice ale acestora, care pot fi validate electronic cu ajutorul unui echipament de detecție, specializat în acest sens.

Următoarea grupă de microparticule este reprezentată de elementele cele mai complexe care pot fi folosite la securizarea hârtiei – microparticule inteligente de tip MHC (metalice holografice codate). Aceste elemente metalice holografice au dimensiunile cuprinse între 50 nm şi 1 mm şi se amplasează pe una dintre suprafețele hârtiei. Conțin un substrat cu o structură de difracție în relief – o imagine holografică, iar printr-o deschidere a elementului metalic (decuparea suportului metalic) se inscripționează un cod alfanumeric de autentificare. Elementele de codare a microparticulei inteligente pot fi identificate cu ajutorul unei lupe sau a unui microscop. Pornind de la aceste date, lucrarea şi-a propus să extindă gama de hârtii securizate folosind ca elemente de securizare nanoparticule din coloizişi pulberi cu proprietăți magnetice.

Noua tehnologie de securizare va avea particularități specifice fiecărui tip de microparticulă care va intra în componența hârtiei (în masă sau la suprafața hârtiei).

În acest fel, cercetarea va oferi producătorului de hârtii şi implicit tipografiilor autorizate în domeniul realizării documentelor de valoare, o varietate mai mare de elemente de securitate bazate pe realizarea unor combinații diverse între indicatorii de securizare sau oferirea întregului sistem. Aceasta deschide posibilitatea obținerii unor soluții particularizate şi unice pentru fiecare document. Pe baza acestor caracteristici, se poate asigura trasabilitatea produsului pentru fiecare lot, plecând de la producătorul de hârtie, tipografia care a realizat documentul şi beneficiarul final al acestuia.

## II. PARTEA EXPERIMENTALĂ

Pentru securizarea hârtiei au fost folosite nanoparticule magnetice de magnetită sub formă de coloid magnetic pe bază de apă şi sub formă de pulberi compozite . Nanoparticulele magnetice sub formă de coloid au fost elaborate prin metoda coprecipitării chimice [Bica et.al. 2007], după care au fost stabilizate cu un strat dublu de acid lauric şi apoi au fost dispersate în apă la o concentrație volumică de ~2% . Pulberile magnetice compozite au fost obținute prin precipitare în prezența ionilor metalici.

Caracterul inovativ al acestor elemente de securitate este dat de unicitatea folosirii lor la nivel național, în structura hârtiei, lărgind astfel aria de utilizare a nanoparticulelor.

Introducerea nanoparticulelor magnetice din coloizi şi din pulberi compozite în compoziția hârtiei s-a realizat în masă, prin tehnici speciale de reținere pe fibră. Astfel se asigură o reținere avansată a acestora în structura hârtiei, obținându-se un efect bun de securizare a hârtiei.

Experimentările au avut ca obiective:

- înglobarea în structura fibroasă a hârtiei a nanoparticulelor magnetice de magnetită din coloid şi din pulberi compozite
- influența lor asupra caracteristicior fizico – mecanice şi de tipărire a hârtiei.

S-au folosit diferite rețete având în compoziție numai amestec din materii prime fibroase la diferite grade de măcinare şi rețete formate din materiale fibroase, materiale de umplere, agenți de retenție şi încleiere , stabilindu-se o compoziție optimă a foilor de hârtie obținute din amestecurile menționate. Pentru experimentări s-au folosit ca *matrii prime fibroase:*

- celuloză sulfat albită fibră scurtă- produsă de Grupul ILIM – Rusia în proporție de 70%
- celuloză sulfat albită fibră lungă- produsă de Bukocel - Slovacia în proporție de 30%

*Materii prime auxiliare:*

- material de umplere - carbonat de calciu
- agent de încleiere – Aquapel
- agentul de retenție – Cartaretin F
- coloid cu proprietăți magnetice dozat în diferite proporții în pastă. Coloidul cu proprietăți magnetice folosit este de tipul - MF/H20, cu densitate: $\rho = 1{,}0779\ g/cm^3$.
- pulberi compozite cu copoziție diferită de magnetită

Celulozele au fost măcinate în holendrul Valley la un grad de măcinare de 38 - 40ºSR pentru celuloză sulfat albită fibră scurtă şi, respectiv, la un grad de măcinare de 42 -45ºSR, pentru celuloză sulfat albită fibră lungă.

S-au realizat seturi de probe din hârtie obținute din paste cu diferite compoziții de materiale fibroase şi auxiliare la diferiete adaosuri procentuale de coloid şi pulberi cu proprietăți magnetice.

Elementul de securizare magnetita sub cele două forme a fost introdusă în suspensia formată din amestecuri de materiale fibroase şi agenți de retenție şi încleiere. Suspensia astfel obținută s-a deshidratat pe aparatul Rapid Kothen, iar foile de hârtie formate s-au uscat la temperatura de 93ºC, timp de 6 min.

# III. REZULTATE ŞI DISCUȚII

### Analiza proprietăților fizico-mecanice ale foilor de hârtie obținute numai din amestec de celuloze

Probele de hârtie oținute prin deshidratarea pastei formată numai din amestec de celuloze cu diferite adaosuri de coloid au fost : P0 – 0% coloid, P1- 1% coloid, P2 – 5% coloid, P3 – 10% coloid, P4 – 25% coloid.

Probele de hârtie astfel obținute au fost condiționate şi analizate fizico – mecanic în Laboratorul de încercări fizico-mecanice al S.C. CEPROHART S.A., acreditat RENAR. Rezultatele obținute sunt prezentate în tabelul 1.

*Tabelul 1 Proprietățile fizico/mecanice ale foilor de hârtie cu diferite adaosuri de coloid*

| Nr.crt. | Caracteristica determinată, UM | Proba de hârtie din amestec de celuloze cu diferite adaosuri de coloid | | | | |
|---|---|---|---|---|---|---|
| | | P0 | P1 | P2 | P3 | P4 |
| 1. | Gramaj, g/m² | 69,7 | 70,5 | 71,3 | 72,7 | 71,1 |
| 2. | Grosime, mm. | 0,098 | 0,098 | 0,101 | 0,101 | 0,100 |
| 3. | Densitate, g/cm³ | 0,71 | 0,72 | 0,71 | 0,72 | 0,71 |
| 4. | Lungime de rupere, m. | 6.293 | 7.030 | 6.940 | 7.007 | 6.769 |
| 5. | Porozitate Gurley, F/S | 115/115 | 129/125 | 138/126 | 128/123 | 125/124 |
| 6. | Grad de alb, % | 56,32 | 39,55 | 33,58 | 27,99 | 21,07 |

Din rezultatele obținute la determinările fizico – mecanice ale probelor de hârtie analizate putem observa următoarele :

1. Adaosul de coloid nu influențează semnificativ caracteristicile fizico – mecanice ale hârtiei idiferent de adaosul de coloid folosit, putem însă observa o uşoară îmbunătațire a caracteristicii – lugimii de rupere, ce evidențiază legaturi slabe între coloid şi matricea celulozică.
2. Pe suprafața activă a amestecului de celuloze coloidul este uşor adsorbit, fenomen evidențiat la dozarea coloidului în suspensia de celuloze la formarea probelor.
3. Retenția coloidului în probele de hârtie analizate bună, analiza colorimetrică a

apelor rezultate la deshidratarea suspensiilor formate din amestecuri de celuloză şi coloid, a evidenţiat acest lucru.

4. Gradul de alb este influenţat semnificativ deoarece culoarea coloidului este brună, cu mărirea adaosului valoarea gradului de alb se micşorează.

Foile obţinute cu adaosuri diferite de de coloid au fost analizate optic la spectrometru Matrix – F, produs de BRUKER OPTICS cu absorbţie în IR apropiat. Rezultatele obţinute sunt prezentate în figura 1.

Valoarea absorbţiei luminii în spectrul IR apropiat creşte odată cu creşterea concentraţiei nanoparticulelor adsorbite pe suprafaţa fibrelor celulozice din hârtie. Această proprietate a nanoparticulelor magnetice folosite ca element de securizare în hârtie lărgeşte aria de detecţie folosită.

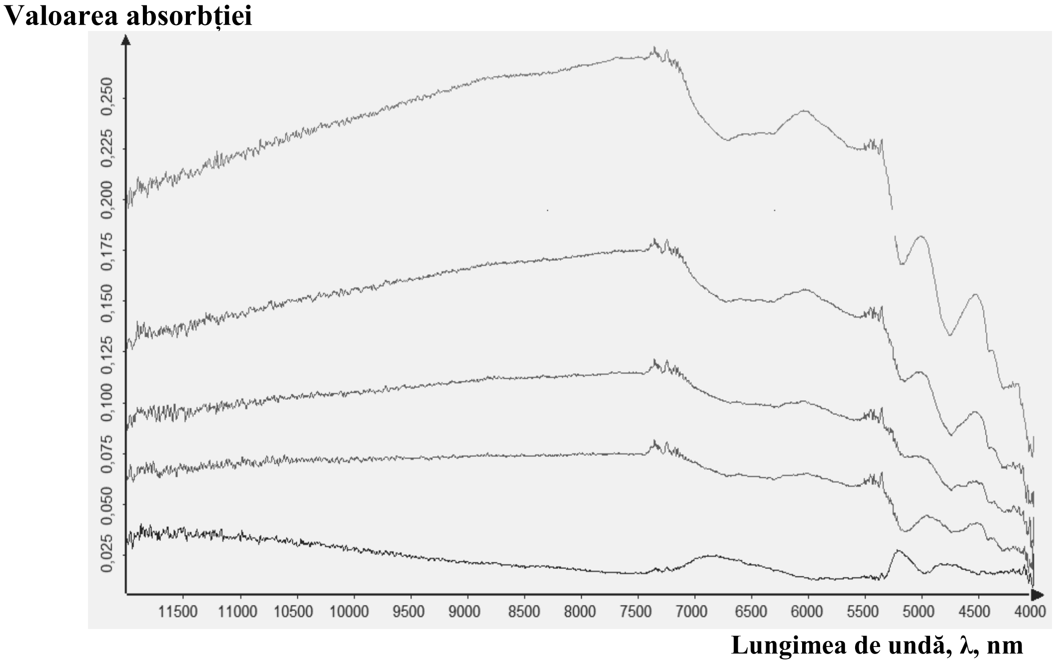


*Fig.1. Curbele de absorbţie a luminii în spectrul IR apropiat*

Pentru a diminua influenţa asupra gradului de alb s-a stabilit utilizarea unui adaos mai mic de coloid sub 1%, care nu va afecta proprietăţile de securizare ale hârtiei. Pentru verificarea acestui adaos şi influenţa lui în proprietăţile fizico - mecanice ale hârtiei s-au realizat cinci seturi de probe în suspensie formate din amestec de celuloze păstrându-se constante caracteristicile materialului fibros folosit, adăugându-se diferite dozaje de coloid în domeniul: 0,1%-0,8%, suspensiile astfel obţinute au fost deshidratate, foile de hârtie obţinute au fost uscate, condiţionate şi analizate fizico-mecanic, rezultatele obţinute sunt prezentate în tabelul 2. Foile de hârtie analizate au avut următoarele adaosuri de coloid: P1/0-0% coloid, P1/1-0,1% coloid, P1/2-0,2% coloid, P1/3-0,4% coloid, P1/4-0,6% coloid, P1/5-0,8% coloid.

*Tabelul 2 Proprietăţile foilor de hârtie tratate cu adaosuri reduse de coloid*

| Nr.crt. | Caracteristica determinată, UM | Proba de hârtie din amestec de celuloze cu diferite adaosuri de coloid | | | | | |
|---|---|---|---|---|---|---|---|
| | | **P1/0** | **P1/1** | **P1/2** | **P1/3** | **P1/4** | **P1/5** |
| 1. | Gramaj, g/m² | 73,1 | 72,6 | 72,9 | 73,2 | 74,6 | 75.9 |
| 2. | Grosime, mm. | 0.114 | 0,113 | 0,114 | 0,113 | 0,114 | 0,118 |
| 3. | Densitate, g/cm³ | 0,64 | 0,64 | 0,64 | 0,65 | 0,65 | 0,64 |
| 4. | Lungime de rupere, m. | 6.493 | 6.600 | 6.540 | 6.607 | 6.769 | 6700 |
| 5. | Porozitate Gurley, F/S | 41/40 | 42/40 | 43/42 | 40/39 | 41/40 | 43/42 |
| 6. | Grad de alb, % | 65,44 | 62,56 | 63,51 | 62,54 | 61,96 | 61,21 |

Din rezultatele prezentate în tabelul 2 se poate observa o scădere mică a gradului de alb cu aproximativ 2-4 unități, în acest domeniu de dozare, caracteristicile fizico-mecanice analizate rămân nemodificate față de rezultatele obținute la analizele inițiale. Rezultatele obținute în acest domeniu al adaosului de coloid, au permis continarea cercetării cu aceste concentrații de nanoparticule magnetice în hârtie. Au fost realizate probe de hârtie obținute prin deshidratarea pastei având următoarea compoziție:

- celuloză fibră scurtă – 70 %
- celuloză fibră lungă – 30
- material de umplere – carbonat de calciu – 15%
- agent de încleiere – Aquapel – 2%
- agentul de retenție – Cartaretin F – 0,5%

Din pasta de hârtie având compoziția menționată s-au realizat 4 seturi de probe cu diferite adaosuri procentuale de coloid cu proprietăți magnetice astfel:

Setul P2/0 fără adaos de coloid, setul P2/1cu adaos de 0,2% coloid, setul P2/2 cu adaos de 0,6% coloid

setul P2/3 cu adaos de 1% coloid

Foile de hârtie obținute cu diferite adaosuri de coloid au fost condiționate şi analizate fizico – mecanic, rezultatele obținute sunt prezentate în tabelul 3.

*Tabelul 3 Proprietățile fizico-mecanice şi structurale ale probelor de hârtie cu adaos de coloid în domeniul 0,2% - 1%*

| Nr. crt. | Caracteristica determinată | UM | Proba de hârtie cu diferite adaosuri de coloid | | | |
|---|---|---|---|---|---|---|
| | | | P2/0 | P2/1 | P2/2 | P2/3 |
| 1 | Gramaj | g/m$^2$ | 77,3 | 79,0 | 76,3 | 76,3 |
| 2 | Grosime | mm | 0,100 | 0,102 | 0,101 | 0,102 |
| 3 | Densitate | g/cm$^3$ | 0,77 | 0,77 | 0,76 | 0,75 |
| 4 | Lungime de rupere | m. | 8725 | 8.408 | 8.396 | 8164 |
| 5 | Porozitate Gurley | F/S | 164/158 | 160/158 | 150/137 | 139/139 |
| 6 | Grad de alb | % | 76,80 | 59,90 | 54,58 | 48,88 |
| 7 | Rezistența la îndoire | | 217 | 277 | 187 | 162 |
| 8 | Absorbția Cobb$_{60}$ | g/m$^2$ | 24,2 | 23,6 | 23,9 | 24,7 |

Adaosul de coloid în acest interval de dozare nu influențează semnificativ caracteristicile fizico – mecanice ale hârtiei obținute. Retenția coloidului în probele de hârtie analizate este mai bună decât retenția din amestecul de celuloze analizat în etapa anterioară observație rezultată din analiza comparativă a scăderii gradului de alb pentru probele cu acelaşi adaos de 1% coloid. Pentru a reduce influența gradului de alb din hârtia securizată magnetic cu element de securizare din coloid s-au sintetizat o serie de compuşi noi obținuți prin precipitarea magnetitei cu diferite metale care au o influență mai mică asupra gradului de alb şi nu influențează în mod semnificativ magnetizația hârtiei. Compuşii denumiți - pulberi compozite au fost obținuți la Academia Romana – Filiala Timisoara, Centrul de Cercetari Tehnice Fundamentale si Avansate, *Laboratorul de Lichide* Magnetice. Aceste pulberi compozite au fost dozate în pasta de hârtie **la un adaos de 0,02% magnetită.**

Rezultatele obținute din analizarea fizico – mecanică a foilor cu adaos de pulberi obținute în laborator sunt prezentate în tabelul 4.

*Tabelul 4 Caracteristicilor probelor de hârtie cu adaos de pulberi compozite*

| Nr. crt. | Caracteristica determinată | UM | Proba de hârtie cu diferite adaosuri de pulberi compozite | | | |
|---|---|---|---|---|---|---|
| | | | P0M | P1M | P2M | P3M |
| 1 | Gramaj | g/m$^2$ | 79,3 | 80,6 | 78,2 | 80,4 |
| 2 | Grosime | mm | 0,112 | 0,115 | 0,111 | 0,118 |
| 3 | Densitate | g/cm$^3$ | 0,71 | 0,70 | 0,70 | 0,68 |
| 4 | Lungime de rupere | m | 7.161 | 6.492 | 6.060 | 6.018 |
| 5 | Porozitate Gurley | Media F/S | 52 | 53 | 47 | 36 |
| 6 | Grad de alb | % | 56,65 | 58,63 | 58,91 | 59,84 |
| 7 | Rezistența la îndoire | Nr. | 370 | 260 | 222 | 181 |
| 8 | Absorbția Cobb$_{60}$ | g/m$^2$ | 29,3 | 33,8 | 34,1 | - |

Din analiza comparativă a valorii gradului de alb observăm o uşoară creştere a acestei caracteristici la aceiaşi cantitate de magnetită - 0,02 % dozată, din aceste rezultate putem aprecia că influența negativă a magnetitei asupra gradului de alb poate fi rezolvată pe această cale.

Caracteristicile fizico - mecanice şi de tipărire ale probelor analizate scad odată cu micşorarea conținutului de magnetită din pulberea dozată, dar pe foile de hârtie obținute având aceste caracteristici se poate tipări.

## Caracterizarea magnetică a probelor de hârtie

Caracterizarea magnetică a probelor de hârtie cu adaos de nanoparticule magnetice de magnetită sub cele două forme a fost realizată de *Centrul National pentru Ingineria Sistemelor cu Fluide Complexe* din cadrul *Universitatii "Politehnica" Timişoara.*"

Magnetizația masică a probelor a fost măsurată prin metoda probei vibrate (Vibrating Sample Magnetometry - VSM) cu un magnetometru VSM 880 (DMS/ADE Techn., USA) la temperatura camerei (~25 ºC).

In figura 2 sunt prezentate curbele de magnetizație masică (emu/$g_{hartie}$) funcție de câmpul magnetic aplicat (A/m) pentru cele 5 probe de hârtie din amestec de celuloze.

Probele de hârtie din amestec de celuloze cu nanoparticule de magnetită (P1 – P4) prezintă o magnetizație de saturație crescătoare, corespunzător cu procentul de coloid magnetic adăugat. Proba P0, fără coloid, prezintă magnetizare. Curba de histereză a magnetizării indică prezența unui material feromagnetic în structura hârtiei, provenind din conținutul de fier al celulozelor folosite, s-a estimat o cantitate de 68 micrograme Fe la 1 gram hartie. Proba P1, cu cel mai mic procent de coloid adaugat (1%), prezintă o magnetizație de saturație semnificativ mai mare decat proba P0.

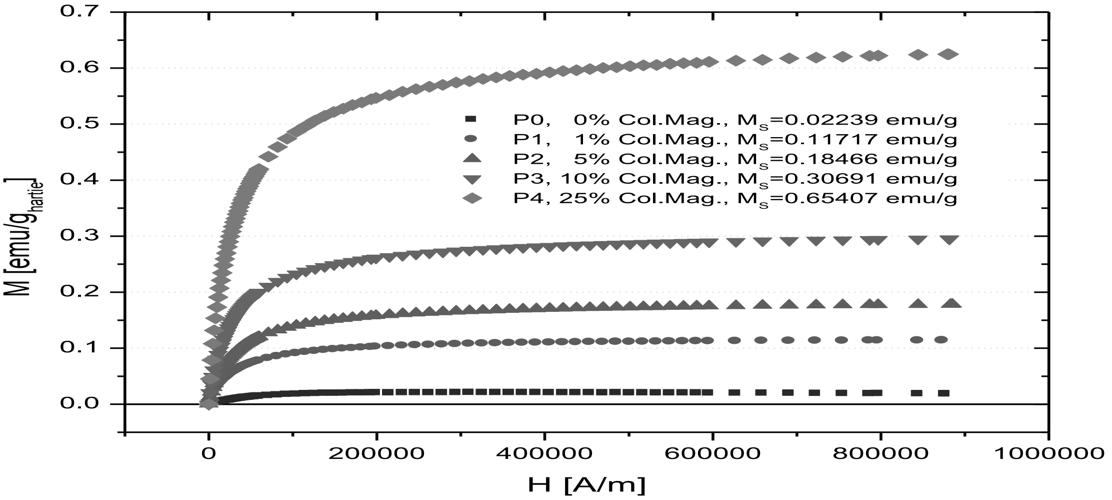


*Fig. 2 Curbele de magnetizație masică pentru hârtie obținută din amestec de celuloze*

În Figura 3 sunt prezentate curbele de magnetizatie masică (emu/$g_{hartie}$) funcție de câmpul magnetic aplicat (A/m) pentru cele 4 probe de hârtie cu retentor. In Figura 4 sunt prezentate curbele de histerezis a probelor în zona de câmpuri mici.

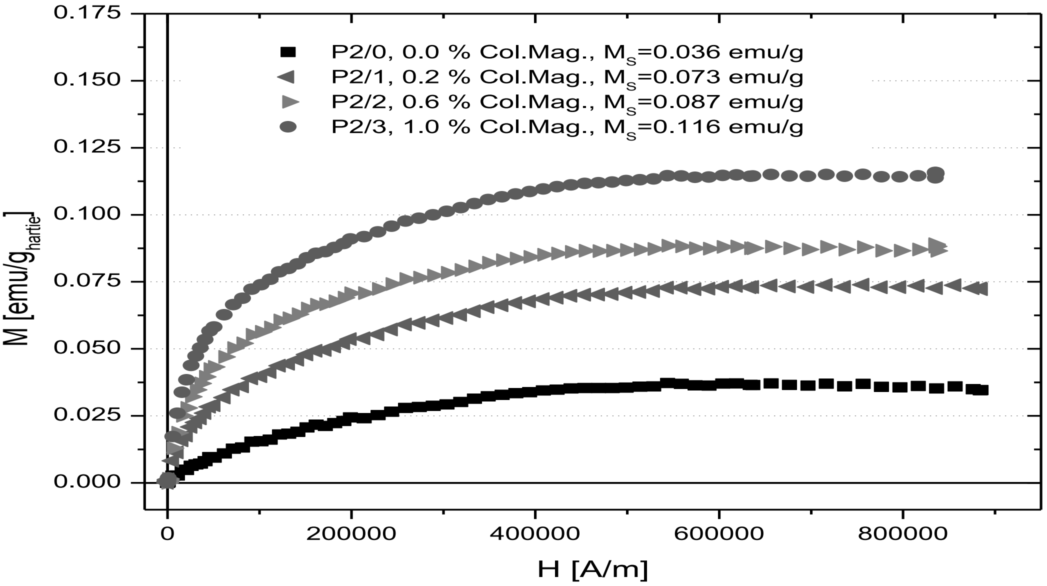


*Fig. 3. Curbele de magnetizaţie masică pentru hârtie cu retentor şi coloid*

Probele de hârtie cu nanoparticule de magnetită (P2/1 – P2/3) prezinta o magnetizatie de saturaţie crescătoare cu procentul de coloid magnetic adăugat. Toate probele prezintă o magnetizare remanentă. Valorile magnetizării remanenete sunt aproximativ egale pentru probele P2/1-3, putin mai mici decât pentru proba P2/0. Având în vedere valorile foarte mici precum si precizia aparatului de măsură, se poate considera că toate probele prezintă aceeaşi magnetizare remanentă. Existenţa magnetizării remanente indică prezenţa unui material feromagnetic în structura tuturor probelor de hârtie, cel mai probabil fier. In ipoteza că fierul monocristalin constituie impuritatea feromagnetică ($M_{sat\text{-}Fe}$=217emu/g), a fost estimată cantitatea de fier din P2.

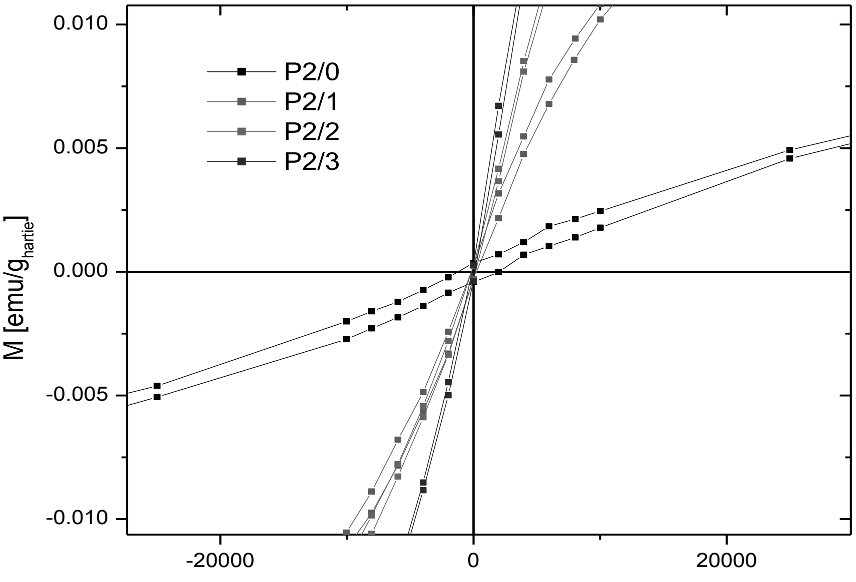


*Fig. 4 Curbele de histerezis*

In Figura 5 de mai jos sunt prezentate curbele de magnetizare masică (emu/$g_{hartie}$) funcţie de câmpul magnetic aplicat (A/m) pentru cele 4 probe de hârtie cu pulberi compozite. In Figura 6 sunt prezentate curbele de magnetizare ale celor trei probe incărcate magnetic (P1,2,3M) din care s-a scăzut magnetizarea probei P0M.

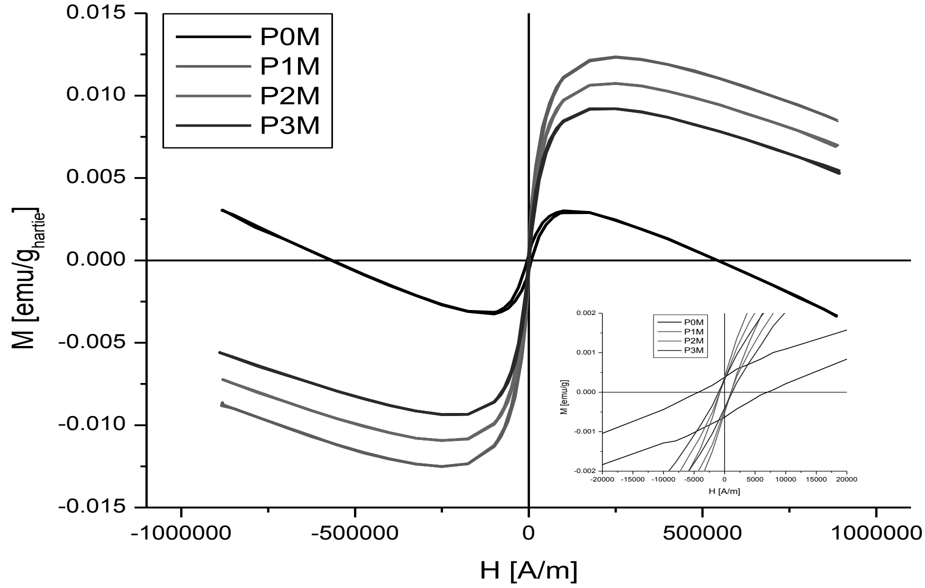


*Fig. 5 Curbele de magnetizaţie masică pentru hârtie cu retentor şi pulberi compozite*

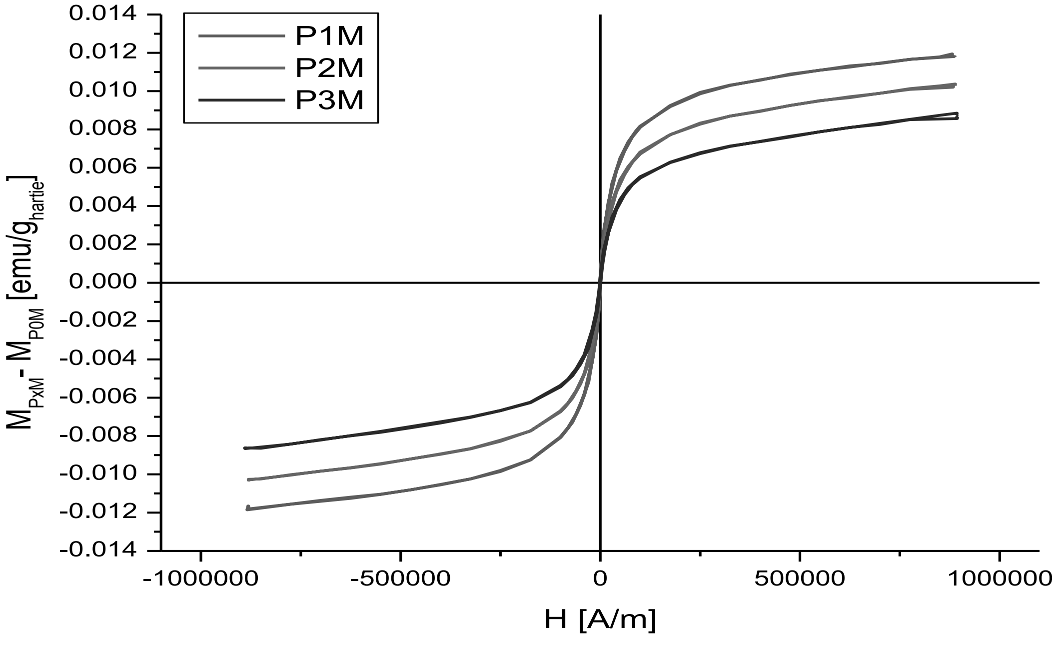


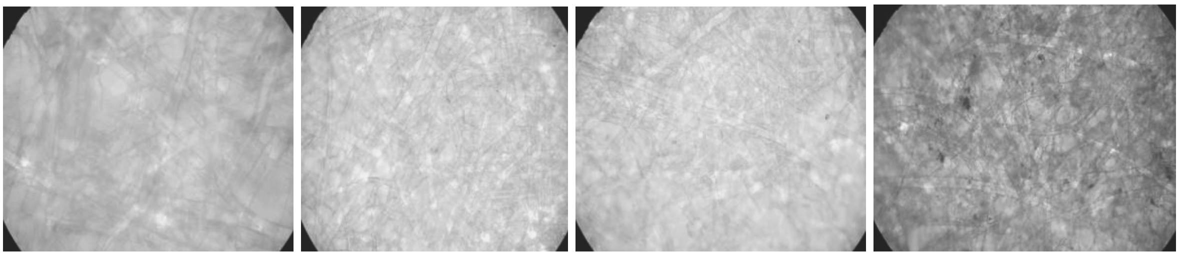
*Fig. 6. Curbele de magnetizaţie masică pentru hârtie cu retentor şi pulberi compozite fără magnetizarea probei P0M*

Probele de hârtie încărcate magnetic cu pulberi compozite (P1M – P3M) prezintă o magnetizaţie de saturatie crescătoare cu gradul de încărcare magnetică a pulberii utilizate (figura 6). Magnetizarea de saturatie a hârtiilor încărcate este foarte mică. Datorită gradului scăzut de încărcare, diamagnetismul celulozei are o pondere semnificativă. Diferenţele dintre magnetizările de saturaţie ale probelor P1-3M si magnetizarea de saturatie a probei P0M nu sunt proportionale cu gradul de încărcare magnetică a pulberii utilizate la elaborare, ceea ce indică o discrepanţă între valorile de încărcare magnetică proiectate şi realizate.

În urma rezultatelor obţinute din analizarea foilor de hârtie cu retentor la un de dozaj de 0,02% magnetită din coloid şi sub formă de pulberi se poate realiza o tehnică de detecţie precum şi un instrument portabil, la nivelul de sensibilitate cerut pentru a detecta semnale în jurul valorii de 0,1 emu/g.

**Analiza microscopică a foilor de hârtie**

Analiza microscopică a foilor de hârtie din amestec de celuloze pentru cele 4 probe analizate au arătat o distribuție uniformă a nanoparticulelor în structura fibroasă a hârtiei, după cum se poate observa în imaginile din figura 7.



P1 P2 P3 P4

*Fig. 7 Structura hârtiilor din amestec de celuloze – imagini la microscop*

## IV. CONCLUZII

- Experimentările au demonstrat că nanoparticulele magnetice de magnetită pot fi utilizate ca elemente de securizare a hârtiilor speciale destinate tipării documentelor de valoare.
- Nanoparticulele nu afectează proprietățile fizico-mecanice ale hârtiei dozate în domeniul de lucru folosit.
- Influența negativă asupra gradului de alb poate fi diminuată prin folosirea pulberilor compozite. Rezultatele obținute din măsurarea caracteristicilor probelor P1M, P2M, P3M au evidențiat acest lucru.
- Datorită dimensiunilor nanoparticulelor pot fi utilizate cantități mici de element de securizare, cercetările au evidențiat acest lucru.
- Randamentul de retenție bun şi distribuția uniformă pe suprafața hârtiei, fac posibilă utilizarea economică a nanoparticulelor. (Fig. 5 Imaginile microscopice)
- Pentru hârtiile care nu necesită un grad de alb ridicat se pot folosi nanoparticulelor din coloid care favorizează formarea de legături chimico-coloidale - nanoparticule – fibre celulozice.
- Prin faptul că nanoparticulele au rezistență chimică, rezistență la temperaturi ridicate şi dimensiuni mici sunt greu distrus.
- Datorită tehnologiei de dozare în masa hârtiei sunt greu de imitat/contrafăcut.
- Securizarea hârtiei folosind nanoparticule asigură trasabilitatea produsului, permite identificarea legală şi în cazul documentelor arse. Supleţea acestei tehnologii este dată de precizie, fiabilitate, productivitate foarte înaltă şi nu în ultimul rând de posibilitatea ridicată de a conduce automatizat procesele defabricație.
- Pentru mărirea randamentului de retenție sunt necesare grade de măcinare mai ridicate ale materiilor prime fibroase utilizate, care conduc la mărirea consumurilor energetice.

**Această cercetare** contribuie la diversificarea sortimentelor de hârtii speciale, grupa de vârf a produselor papetare, prin realizarea unui nou element de securizare a hârtiilor destinate obținerii documentelor de valoare a căror autenticitate se poate verifica în viitor concomitent prin două metode: detecție magnetică şi detecție optică - cu ajutorul radiațiilor UV.

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# POLYSACCHARIDES UTILIZATION FOR WATER DECONTAMINATION

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## Abstract

Industrial water represents an important factor of pollution. In this context, we wanted to conduct a study on the retention of pollutants from water on the surface of certain polysaccharides. These polysaccharides were cellulose and derivates obtained by chemical modification of cellulose into: CMC and AC. The study involves analysis of wastewater before and after filtration. Filtration was realized with a filter on which surface was polysaccharides. Measurements pursued were: analysis of sulphides, chlorides (Mohr method), cyanide (titrimetric method by Tyndall effect) and determination of pH. The results obtained showed that each of the cellulose derivates appears to be specific for the retention of certain pollutants, as follows: cellulose and AC retain the sulphides, chlorides are retained in the largest amount by AC, and CMC retains largest quantity of cyanide. pH of polluted water, which was initially at weak base (pH = 8.36) was influenced by filtration through polysaccharides studied, changing his value (8.11 after filtration with CMC, 7.98 after filtration with AC and 7.74 after filtration with cellulose). The results show that the polysaccharides studied have the ability to retain from water the pollutants studied. Chemical modification of cellulose has a positive influence on the capacity of retention, especially of cyanide, in a proportion of more than 80%.

**Keywords**: Waste waters, Polysaccharides, Filtration, Pollutants

## Rezumat

Apa este o resursă critică şi nevoia de resurse de apă dulce din întreaga lume va deveni din ce în ce mai critică, pe măsură ce populaţia lumii creşte şi apar schimbările climatice [1]. Activitatea umană influenţează mediul şi natura într-un mod negativ şi în mai multe feluri [2]. Cercetarea în diferite domenii privind resursele de apă, cum ar fi: managementul, politica, poluanţii din surse difuze, apele uzate, nutrienţii şi calitatea apei a crescut semnificativ în ultimii ani [1, 3]. Apa industrială reprezintă un factor important de poluare, motiv pentru care au fost realizate mai multe programe pentru reducerea cantităţilor de ape uzate [4, 5]. În literatura de specialitate au fost raportate cercetări privind decontaminarea apei folosind diferiţi derivaţi de celuloză, cum ar fi: celuloză dietilaminoetil (DEAE), acetat de celuloză (CA), sodium carboximetilceluloză (CMC) şi, de asemenea, celuloză. S-a raportat, de asemenea, eliminarea cu succes a coloranţilor [6, 7], a metalelor bivalente [8-10] şi a metalelor grele [11]. În acest context, ne-am dorit să dezvoltăm un studiu referitor la retenţia poluanţilor din apă pe suprafaţa anumitor polizaharide. Aceste polizaharide sunt celuloza şi derivaţii obţinuţi prin modificarea chimică a celulozei în: CMC şi AC[12]. Studiul implică analiza apelor uzate înainte şi după filtrare. Filtrare a fost realizată cu un filtru cu polizaharide. Măsurătorile urmărite au fost: analiza de sulfuri, cloruri (metoda Mohr), cianuri (metoda tritrimetic cu efect Tyndall) şi determinarea pH-ului. Rezultatele obţinute au arătat că fiecare dintre derivaţii de celuloză par să fie specifici pentru retenţia anumitor poluanţi, după cum urmează: celuloză şi AC păstrează sulfuri, clorurile sunt cel mai bine reţinute de AC, iar CMC-ul păstrează cea mai mare cantitate de cianură. pH-ul apei poluate, care a fost inițial bază slabă (pH = 8.36) a fost influențat de filtrarea prin polizaharidele studiate, schimbându-şi valoarea (8,11 după filtrare cu CMC, 7,98 după filtrare cu AC şi 7,74 după filtrare cu celuloză). Rezultatele arată că polizaharidele studiate au capacitatea de a reține din apă poluanții studiați. Modificarea chimică a celulozei are o influență pozitivă asupra capacității de retenție, în special a cianurii, într-o proporție mai mare de 80%.

**Cuvinte cheie**: Ape uzate, Polizaharide, Filtrare, Poluanți

# I. INTRODUCTION

Water is a critical resource, and the shortage of freshwater resources worldwide will only become more critical as the world population increases and climate changes [1]. Human activity adversely affects nature in many forms [2]. In the last 20 years, research in various domains concerning water resources such as: management, politics, pollutants from diffuse sources, wastewaters, nutritive substances and water quality has gone up significantly over the past 20 years [1, 3]. Industrial water represents a very important pollution factor, grounds on which several programs to reduce it have been made [4, 5]. Management of water resources offers a multitude of challenges and depending on the progression of science, technology and policy making, requires integrated closeness for it to be successful [1]. The importance of freshwater availability was realized through the UN's General Secretary press release concerning the International Water Day in 2002. "It is estimated that approximately 1.1 billion people do not have access to drinkable water, 2.5 billion don't have access to sewerage and more than 5 million people die each year due to diseases related to water sanitation, these numbers being on average 10 times bigger of those killed in wars. Most often water is viewed like a infinite free good. Nevertheless, even if deliveries are sufficient or abundant, the risk of pollution and demand go up. By the year 2025 two thirds of the World's population could be residing in countries with moderate or severe water deficits" [6]. In literature there have been reported research regarding depollution of water using cellulose derivatives, like diethylaminoethyl cellulose (DEAE), cellulose acetate (CA), carboxymethyl cellulose (CMC) and cellulose, registering success in removing dyes [7, 8], some bivalent metals (Fe, Ni) [9, 10, 11] and some heavy metals (Cu, Pb) [12]. Wastewaters from the chemical industry contain among liquid particles and insoluble solids numerous organic components and inorganic soluble [13].

In the present work is showed a study of retaining sulphides, chlorides and cyanide ions towards a efficient depollution with the help of three polysaccharides : cellulose, cellulose acetate (CA) and carboxymethyl cellulose. The sulphides, cyanides and cyanide ions are but a few of the pollutants that present a negative effect on human health [14, 15, 16], and concurrently lead to critical problems in the sewerage systems [14].

The water's pH is described as "an important variable" to many physical and biological processes in natural [17] on account for the study includes the pH analysis of polluted water from the chemical industry.

# II. EXPERIMENTAL

## 2.1. Water preparation

Analyses were done on residual waters from the chemical industry.

The polluted waters were filtered through a layer of polysaccharide, after which the fallowing tests were done: determination of the content of sulphides, cyanides and cyanide ions and determination of the pH.

## 2.2. Analyses of sulphides

The method used for the determination of sulphides content in used water corresponds to STAS: SR 7510:1997 *This reproduction was made with the consent of Standardization Association of Romania – ASRO nor. LUC/13/161 of 29.07.2013.*

The content of sulphates is expressed in milligrams per litre and is calculated with the formula that corresponds to SR 7510:1997

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$$Sulfuri(S^{2-}) = (V_1 \cdot f_1 - V_2 \cdot f_2) \cdot 0.1 \cdot 16.04 \cdot \frac{1000}{V}$$

[mg/ l]

V – volume of water sample used for analysis;
$V_1$ – volume of iodine solution used for determination, (ml);
$V_2$ – volume of $Na_2S_2O_3$ solution used for titration, (ml);
$f_1$ – factor iodine solution;
$f_2$ – factor $Na_2S_2O_3$ solution;
N – normality of iodine and thiosulphate solutions;
16,04 – quantity of sulphides corresponding to 1 ml of iodine solution N (mg).

For dilutions, the relation is multiplied by the dilution ratio r = $V_3$/ $V_4$, where:
$V_3$ – volumetric flask volume in which the dilution is made, (ml);
$V_4$ – volume of sample, (ml);

### 2.3. Determination of cyanide ions – Tyndall method

The protocol used for cyanide ions determination corresponds to STAS: SR ISO 6703-1:1998 *This reproduction was made with the consent of Standardization Association of Romania – ASRO nor. LUC/13/161 of 29.07.2013*.

The calculation for determination of total cyanide concentration, expressed in milligrams per litter is given by the formula according to SR ISO 6703-1:1998 *This reproduction was made with the consent of Standardization Association of Romania – ASRO nor. LUC/13/161 of 29.07.2013*:

$$CN^- = \frac{(V_1 + V_2 - V_0) \cdot f_1 \cdot 1000}{V}$$

$V_0$ –total volume (ml) of Ag $NO_3$ solution used for two titration of blank;
$V_1$ – volume (ml) of $AgNO_3$ solution used for first titration;
$V_2$ – volume (ml) of $AgNO_3$ solution used for second titration;
V – volume (ml) of sample;
$f_1$ = 0,052, mass (mg) of $CN^-$ equivalent to 1 ml of $AgNO_3$ solution to 0.001 mol/l;

### 2.4. Analysis of chlorides content (Mohr method)

Working method used for the determination of chlorides is described in SR ISO 9297:2001 *This reproduction was made with the consent of Standardization Association of Romania – ASRO nor. LUC/13/161 of 29.07.2013.*

The calculation for the determination of chloride in polluted water, complies SR ISO 9297 :2001 *This reproduction was made with the consent of Standardization Association of Romania – ASRO nor. LUC/13/161 of 29.07.2013*:

$$\rho_{Cl} = \frac{(V_s - V_b) \cdot c \cdot f}{V_a}$$

where:

$\rho_{Cl}$ –chlorides concentration, (mg/ l);
$V_a$ – volume of sample to be analysed, (ml);
$V_b$ – volume of $AgNO_3$ solution used for titration of blank, (ml);
$V_c$ – volume of $AgNO_3$ used for titration of sample, (ml);
c – actual concentration of $AgNO_3$ solution (moli/ l);
f –conversion factor; f = 354453 mg/ mol;

## III. RESULTS AND DISCUSSIONS

### 3.1. The content of pollutants retained by polysaccharides

The wastewater studied contains: 243,808 mg/ l sulphides, 560,866 mg/ l chlorides and 9,152 mg/ l cyanides.

The results of analysis of pollutants are plotted in the figure 1.

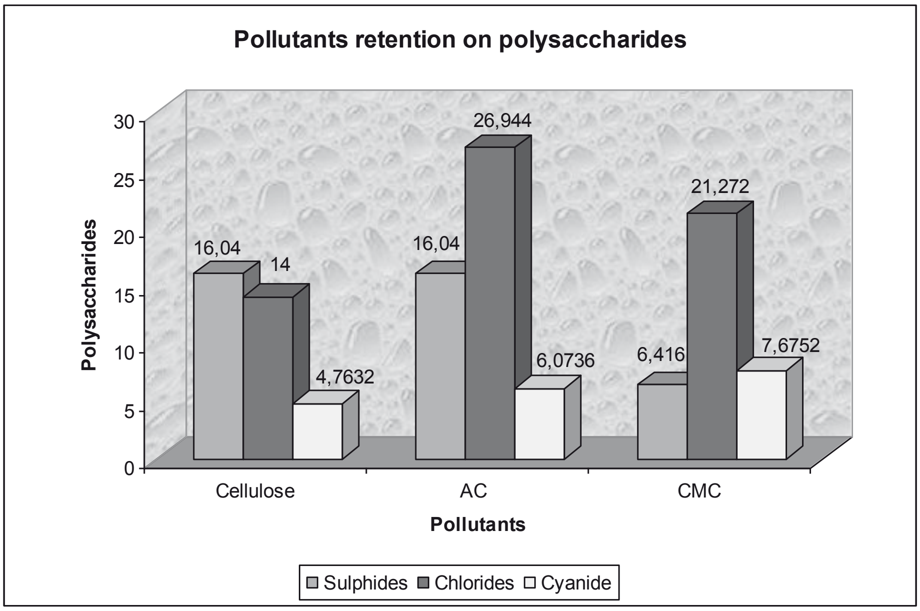

*Fig.1 Pollutants retention on polysaccharides*

It can be observed that the polysaccharides that retain the largest quantity of sulphides are cellulose and the cellulose acetate (CA) – 16,04 mg/ 1. Carboxymethyl cellulose (CMC) retained only 6,416 mg/ 1. Taking into account that the substitution degree (DS) of CA is 1,83 [18], it results that unmodified cellulose exists and it influence therefore the retaining of sulphides. The CMC retained sulphides in a low quantity therefore resulting that the group of carboxymethyl unfavores the retaining of sulphides on the surface of the polysaccharide.

The highest content of chlorides was retained by CA 26,944 mg/ l, followed by CMC with 21,272 mg/ l and cellulose that retained only 14,182 mg/ l. Therefore it can be said that the acetate grouping (-$CH_2$-CHO) which replaces H from the grouping –OH of cellulose influences in a positive way the retaining of chlorides and such a bond forms with greater ease between the $Cl^-$ ion with the grouping –$CH_2$-CHO than the grouping –$CH_2$-COONa. Because the carboxymethyl grouping (-$CH_2$-COONa) contains an extra O, in addition to the acetate grouping and the chlorine combines itself directly with all elements but oxygen [19], we assume that the very absence of this Oxygen determines the retaining of chlorides on CA.

Results obtained showed that cyanides were retained in the highest proportions of CMC – 7,675 mg/l while CA retained 6,073 mg/ l and cellulose only 4,763 mg/ l. Table 1 renders the procentual quantity of pollutants retained by each polysaccharides.

*Table 1 Quantity of pollutants retained by polysaccharides, in %*

| Nr. crt. | Polysaccharide | $S^{2-}$ (%) | $Cl^-$ (%) | $CN^-$ (%) |
|---|---|---|---|---|
| 1. | Cellulose | 6,57 | 2,53 | 52,04 |
| 2. | AC | 6,57 | 4,8 | 66,36 |
| 3. | CMC | 2,63 | 3,79 | 83,86 |

Studies made show that CA retains the greatest quantity of chlorides 4,8%, CMC retains 83,86% cyanides and the greatest quantity of sulphides is retained by cellulose and CA. Therefore it looks like the acetate grouping (-$CH_2$-COH), and the carboxymethyl grouping (-$CH_2$-COOH) that replace the H from the –OH grouping of cellulose present a certain attraction for a certain type of pollutant: chlorides in CA case and cyanides in the case of CMC.

### 3.2. The influence over pH

Studies performed have demonstrated that polysaccharides can influence in a small manor, the pH of polluted water. The quantity of polysaccharide through which filtration was achieved was 3g. Therefore from an initial pH of 8,36 of the polluted water it dropped down to 7,74 when it was filtered through cellulose, 7.98 after filtration through CA and 8,11 when filtered through CMC. Polysaccharides have presented a small sensibility of pH, its values staying the same in a weak base domain.

## IV. CONCLUSIONS

The present article had to purpose of tracking the retaining of pollutants on the surface of various polysaccharides: cellulose, cellulose acetate and carboxymethyl cellulose. Results show that CMC retains 83,86% cyanides, CA retains on its surface sulphides (5,96%) and chlorides (4,8%) and cellulose retains the largest quantity of sulphides (5,96%)

Depollution of waters with the help of polysaccharides has been proved to be efficient through the use of CMC to remove over 80% of cyanide ions. The pH of the polluted water being initially in a weak base domain (8,36) has suffered modifications after the filtration of the water through polysaccharides.

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# SECURIZAREA HÂRTIEI CU MICROPARTICULE DE TIP *METAL/TiO$_2$*

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## Rezumat

În această lucrare sunt prezentate rezultatele cercetărilor experimentale la nivel de laborator, pentru sintetizarea unui element de securizare a hârtiei de tip metal/TiO$_2$ cu proprietăți magnetice şi implementarea lui în matricea hârtiei. Lucrarea prezintă metodologia de securizarea a hârtiei, care se desfăşoară în două etape. Prima etapă constă în sintetizarea elementului de securizare cu proprietăți magnetice în cadrul SC Ceprohart SA, prin combinarea metodelor de coprecipitare şi hidrotermală. Microparticulele metal/TiO$_2$ obținute conțin 0,9% component dopant şi au fost caracterizate prin analize specifice în vederea introducerii în masa hârtiei: compoziție granulometrică, densitate specifică, comportare în mediu apos. A doua etapă prezintă introducerea microparticulelor magnetice sintetizate în masa hârtiei. Rezultatele vor fi discutate pe larg pentru a demonstra posibilitatea utilizării acestor elemente la securizarea hârtiei.

**Cuvinte cheie:** Hârtie securizată, Microparticule, Proprietăți magnetice, Element de securizare

## Abstract

In this paper are presented the first results of experimental researches in CEPROHART's laboratories, for synthesizing of a security element for paper, type Me/TiO$_2$ with magnetic properties and the introduction of this element in the matrix of the paper. This paper presents the methodology of securing the paper, which occurs on two stages. The first stage consists in synthesizing of security element with magnetic properties inside, by a combination of co-precipitation and hydrothermal methods. The obtained micro particles of Me/TiO$_2$ contain 0.9% magnetic component and were characterized by specific analyses before to be introduced in the paper. Were checked: the particles size, specific density, behaviour in aqueous medium. The second stage presents the introduction of synthesized magnetic micro particles in the paper. The results demonstrate the possibility to secure the paper by transferring some particular magnetic properties.

**Keywords:** Security paper, Microparticles, Magnetic properties, Security element

# I. INTRODUCERE

Fabricarea hârtiilor securizate constitue un segment important în industria de hârtie nu atât prin ponderea producţiei, cât datorită gradului de complexitate şi importanţa strategică pe care o are. Toate hârtiile de valoare au în comun conceptul de securitate. Acesta este garantat de cele două elemente de bază: hîrtia şi tiparul, fiecare asigurând în proporţii variabile, de la caz la caz, caracteristici de securitate care garantează autenticitatea şi descurajează falsificarea.

Tehnologiile şi tehnicile de realizare a acestor hârtii securizate sunt ținute în secret de către fabricanți. De aceea, producătorii de astfel de hârtii îşi realizează un concept propriu pentru fabricarea hârtiilor securizate [1]. În acest sens, s-a realizat un sistem integrat propriu de securizare, care cuprinde tehnologii de fabricare a hârtiilor securizate cu diverse elemente de securizare sau combinații ale acestora, în funcție de cerințe [2].

Obținerea elementului de securizare în cadrul SC Ceprohart SA Brăila reprezintă un avantaj atât din punctul de vedere al sistemului de securizare a documentelor cât şi al aspectelor economice. În plus, elementul de securizare de tip metal/$TiO_2$, face parte din categoria elementelor introduse în matricea hârtiei, fiind închise sau ascunse, cunoscute numai de către emitent şi poate fi detectat numai cu ajutorul unor echipamente speciale, care vor fi studiate [3].

Sinteza şi caracterizarea microparticulelor a devenit un domeniu interdisciplinar de mare interes în ultimul deceniu datorită aplicațiilor industriale pe care le prezintă. Microparticulele sunt particule ultrafine cu dimensiuni mai mici de 1$\mu$m. Totuşi, definiția microparticulelor variază în funcție de material, domeniu sau aplicație. Etapa de sinteză a microparticulelor este deosebit de importantă deoarece proprietățile microparticulelor depind în mare măsură de dimensiunea acestora [4]. Aceste microparticule prezintă proprietăți chimice, magnetice, optice şi mecanice diferite de ale materialului cu granulație convențională [6].

De multă vreme dioxidul de titan este utilizat ca material de umplere la fabricarea hârtiei şi sub forma unor acoperiri în cazul hârtiilor cretate[7]. Dioxidul de titan (tianina) şi micropulberile pe bază de tianină au atras atenția în ultima vreme nu numai interesului ştiințific dar şi aplicațiilor în diverse domenii ale acestora ( sănătate, industria sticlei, hârtiei, constructoare de autoturisme, vopselelor, alimentară, cosmetică, protecția mediului şi apratură de detecție, etc.). Aşadar, prin încorporarea microparticulelor de tip metal /$TiO_2$ în matricea hârtiei se poate asigura securizarea datorită proprietăților magnetice pe termen lung [6]. Retenția acestora în structura hârtiei se realizează ca şi la materialul de umplere prin filtrare pentru microparticulele mai mari si prin fenomene coloidale pentru microparticulele ultrafine [7].

Scopul acestei lucrări a fost investigarea sintezei şi caracterizarea micropulberilor de tip metal /$TiO_2$ utilizând combinarea a două metode, coprecipitare şi hidrotermală. Aceste metode oferă o serie de avantaje: necesită manipulare minimă, aparatură simplă, temperatură de sinteză scăzută, materii prime ieftine, control uşor al dimensiunii, precum şi omogenitate chimică excelentă a produsului final. Aşadar metodele de coprecipitare şi hidrotermală sunt indicate în sinteza metal/$TiO_2$ la temperaturi joase şi cu grad de puritate înalt. Principalul dezavantaj constă în faptul că procesul este limitat la soluțiile cationilor cu produşi de solubilitate similari[9]. Materiile prime utilizate în mod frecvent sunt: hidroxizi, carbonați, nitrați, sulfați. Este cunoscut faptul că în solide morfologia şi microstructura particulelor depind atât de natura precursorului cât şi de parametri experimentali ai întregului proces, mai precis dimensiunea particulelor poate fi controlată prin simpla varietate a condițiilor experimentale [6,8].

Prin utilizarea acestui proces este posibilă obținerea micropulberilor de tip M/$TiO_2$ care pot fi utilizate ca element de securizare cu caracteristici magnetice în securizarea hârtiei.

# II. PARTEA EXPERIMENTALĂ

## 2.1. Materiale

Reactivii utilizați în lucru au fost de puritate analitică şi au fost folosiți ca atare fără nici o purificare prealabilă. Soluțiile apoase au fost preparate cu apă distilată.

## 2.2. Prepararea probelor

Microparticulele de tip metal/$TiO_2$ au fost obținute prin combinarea metodelor coprecipitare – hidrotermală. Metoda de sinteză are loc în două etape: obținerea precursorului prin metoda de coprecipitare şi respectiv formarea micropulberilor de tip metal/$TiO_2$ prin metoda hidrotermală respectiv descompunere termică.

S-a preparat separat o soluție apoasă de sare dopantă corespunzătoare şi o suspensie apoasă de $TiO_2$ dispersată corespunzător. S-au amestecat la temperatura camerei cu un agitator, după care amestecul a fost introdus sub agitare în baia de apă, unde se menține un interval de temperatură cuprins între 85-95ºC. S-a adăugat în picături o soluție atât pentru precipitarea fiecărei specii cationice cât şi pentru reglarea pH-ului de reacție (6-8). Precipitatul format a fost filtrat, spălat cu apă distilată şi uscat în aer, timp de 24h la 40ºC. Micropulberile de tip metal/$TiO_2$ au fost obținute prin calcinarea precipitatelor uscate într-un creuzet de platină la temperatura de 450ºC, timp de 4h, în aer, la presiunea atmosferică. Pulberea obținuta are culoarea galben pal.

Sărurile dopante utilizate au fost $Fe_2(SO_4)_3 \cdot 5H_2O$; $Fe(NO_3)_3 \cdot 9H_2O$ şi $FeCl_3 \cdot 6\,H_2O$. Soluția de precipitare (pH 6-8), a fost preparată prin dizolvarea în apă distilată a cantităților adecvate de hidroxid de sodiu, carbonat de sodiu şi un adaos de precipitare specific fiecărui element.

Descompunerea termică s-a efectuat într-un cuptor de calcinare.

### 2.3. Caracterizare

Micropulberile obținute au fost caracterizate prin analize specifice, în vederea introducerii în structura hârtiei. Se ştie că hârtia se obține în mediu apos prin procedeul de încleiere în mediu alcalin. Caracterizarea micropulberilor obținute: determinarea densității aparente, compoziție granulometrică prin metoda sedimentării, microscopie de forță atomică în modul non-contact (NCAFM), compactizarea microparticulelor în conformitate cu diagramele Eh - pH. Toate măsurătorile au fost efectuate la temperatura camerei.

### 2.4. Caracterizarea hartiei securizate cu micropulberi de tip Fe/$TiO_2$

Hârtia reprezintă o structură fibroasă care adeseori înglobează şi materiale auxiliare şi are anumite proprietăți impuse de domeniul de utilizare [5].

Pentru testarea proprietăților de securizarea a hartiei cu microparticule de $TiO_2$ dopate cu Fe au fost utilizate foi de laborator, atât pentru caracterizarea hârtiei obținute cât şi pentru determinarea proprietăților feromagnetice a componentului Fe/$TiO_2$. S-a stabilit reteta de lucru pentru pasta de hartie (rețeta martor) cu respectarea urmatoarelor faze de formare a foilor: destramare, individualizare, macinare, umplere, incleiere, retenție, formare şi uscare. Microparticulele de Fe /$TiO_2$ au fost introduse în pasta de hartie ca şi material de umplere (rețeta Fe/$TiO_2$ ). Creşterea randamentului de retenție a microparticulelor s-a realizat prin introducerea unor aditivi chimici în pasta de hârtie. Retenția microparticulelor şi adaosul de microparticule de Fe/$TiO_2$ determină: densitatea şi distribuția acestora în foaia de hartie şi feromagnetismul hârtiei. Foile de laborator au fost caracterizate fizico-mecanic, după păstrarea lor în atmosferă condiționată. Atât fazele de laborator, cât şi analizele fizico-mecanice s-au efectuat în conformitate cu normativele în vigoare [10].

Pentru testarea proprietăților feromagnetice a microparticulelor de Fe/$TiO_2$, a fost utilizată ca etalon rețeta martor ($A_1$) şi foi de laborator cu adaos de 0,2g/kg hârtie microparticule de Fe/$TiO_2$, cu diferite grade de dopare 0,9; 1,2 şi 5% (rețetele $A_2$; $A_3$; $A_4$). Prezența feromagnetismului s-a realizat prin măsurarea curbelor de magnetizare remanentă a foilor de laborator prin metoda probei vibrate (Vibrating Sample Magnetometry - VSM) cu un magnetometru VSM 880 (DMS/ADE Techn., USA) la temperatura camerei (~25 ºC). [12].

## III. REZULTATE ŞI DISCUȚII

### 3.1. Caracterizarea microparticulelor de tip Fe/$TiO_2$

Pentru determinarea compoziției granulometrice s-a utilizat metoda sedimentării după legea lui Stokes (Tabelul 1). Acest studiu constă în măsurarea variației în timp a concentrației în particule a suspensiei la un nivel de referință din vas, prin prelevarea unor probe de suspensie. Concentrația în particule a probelor prelevate se face prin măsurarea masei de granule din probă şi raportarea ei la volumul probei. Dimensiunea microparticulelor a fost confirmată de microscopia de forță atomică non-contact (NCAFM) de topografie 3D pentru proba de $TiO_2$ dopat cu 0,9%Fe (Figura 1).

*Tabelul 1 Compoziția granulometrică a microparticulelor Fe/$TiO_2$*

| Nr.crt. | Dimensiunea particulelor | UM | Compoziția Fe/$TiO_2$ |
|---|---|---|---|
| 1. | Particule 0,2μm (200 nm) | % | 6,8 |
| 2. | Particule 0,5μm (500 nm) | % | 41,5 |
| 3. | Particule 0,8μm (800 nm) | % | 40,3 |
| 4. | Particule 1μm (1000 nm) | % | 10,8 |

În tabelul 1 sunt date valorile compoziţiei granulometrice. Mărimea particulelor se încadrează în limitele specifice particulelor de dimensiuni nano.

Microscopia de forţă atomică non-contact a evidenţiat, pentru ambele probe de Fe/$TiO_2$ sub formă de filme subţiri, existenţa unor formaţiuni aproximativ circulare cu diametru de 0,75µm şi respectiv 406 nm. Aceste formaţiuni ar putea fi considerate ca fiind datorate unor aglomerări ale ionilor de Fe.

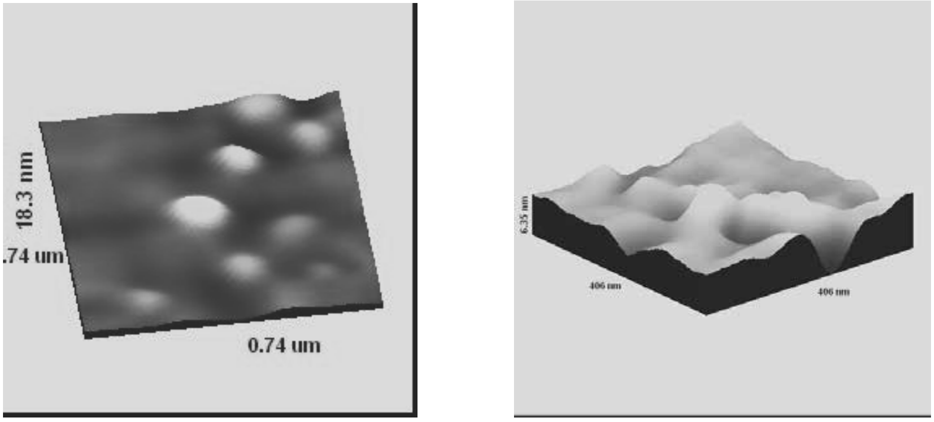

*Fig. 1 Imagini NCAFM de topografie 3D pentru proba TiO2 dopat cu 0,9% Fe*

La o mărime redusă, se remarcă formaţiuni de agregare din particule foarte fine care însă se dispersează la cea mai mică solicitare. Temperatura redusă a tratamentului termic opreşte creşterea cristalitelor generând materiale foarte fine.

Pentru a cunoaşte comportarea în suspensie a microparticulelor Fe/$TiO_2$, comparativ cu fibrele celulozice, s-a determinat densitatea acestora exprimată prin raportul dintre greutatea şi volumului ocupat de microparticule (t = 20°C). În tabelul 2 se prezintă densitatea microparticulelor Fe/$TiO_2$, comparativ cu densitatea hârtiei [9]:

*Tabelul 2 Densitatea microparticulelor comparativ cu hârtia*

| Nr.crt. | Sortiment | Densitatea, kg/$m^3$ |
|---|---|---|
| 1. | Microparticule Fe/$TiO_2$ | 800 - 900 |
| 2. | Hârtie | 700 - 1300 |

Rezultatele celor două densităţi sunt apropiate, evidenţiindu-se compatibilitatea lor în structura hârtiei. Interesul pentru determinarea modului de stabilitate a microparticulelor Fe/$TiO_2$ într-un sistem apos (obţinerea hârtiei), a condus la investigarea diagramelor Eh-pH (diagrama Pourbaix), pentru $TiO_2$ – figura 2. Diagramele Eh-pH sunt instrumente utile pentru vizualizarea zonelor de stabilitate ale speciilor de ioni metalici într-o soluţie, în funcţie de activitatea ionilor de hidrogen (pH) şi activitatea de electroni (Eh), în medii naturale. Aceste diagrame pot fi folosite pentru a indica modul în care diferiţi ioni metalici pot fi separaţi unul de altul prin efectuarea de modificări în aceste variabile (după Nordstrom and Munez, 1985).

În diagramă liniile punctate reprezintă zone de stabilitate a apei, adică zona de relevanţă pentru mediu apos. Linia superioara (b) reprezintă echilibrul dintre apă şi oxigen. Dacă soluţia are potenţialul crescut peste linia punctată, apa este oxidată cu formarea ionilor de oxigen şi hidrogen. Linia inferioară (a) indică, cazul în care ionii de hidrogen într-o soluţie sunt reduşi la gaz de hidrogen.

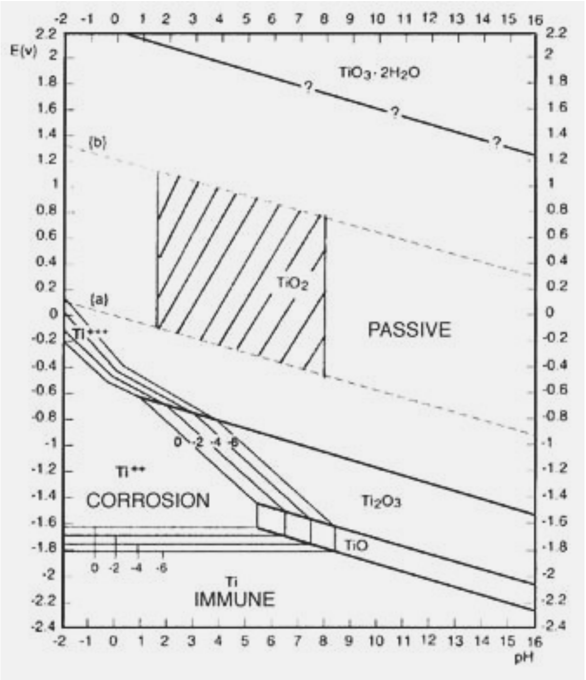

*Fig. 2 Diagrama de stabilitate Eh-pH pentru $TiO_2$*

În figura 2 diagrama Eh-pH, confirmă stabilitatea dioxidului de titan dopat cu Fe în în intervalul de pH: 2 - 8 (zona haşurată). Efectul „inactiv”, este dat de formarea stratului de oxid în jurul metalului, strat care acoperă suprafaţa metalului, asigurand protecţia. Se poate observa că intervalul de pH: 2 - 8 coincide cu cel de obtinere a hartiei prin procedeul neutru/slab alcalin (pH-ul pastei de hartie este cuprins intre 6,5 şi 8,5).

### 3.2. Obţinerea hârtie cu microparticule $Fe/TiO_2$

În urma testelor de laborator s-a stabilit reţeta de lucru. Aceasta conţine material fibros şi auxiliar în anumite proporţii, specifice unei reţete de fabricaţie a hârtiilor securizate. În plus, a fost introdus în procesul de măcinare un aditiv chimic pentru facilitarea reţinerii materialului fin - microparticulelor de tip $Fe/TiO_2$ în masa hartiei. Reţeta martor este:

- conţinut de celuloză sulfat înălbită din răşinoase – 20 – 40 %
- conţinut de celuloză sulfat înălbită din foioase – 60 – 80 %.

Faţă de acest amestec fibros se adaugă:

- material de umplere (carbonat de calciu) – 8 - 20 %;
- agent de încleiere (alchil dimercetone) – 1 - 2 %;
- agent de retenţie (poliamin-poliamid-epiclorhidrină) – 0,5 - 1,5 %.

În urma experimentărilor s-a selecţionat reţeta cu adaosul de 0,2g / kg hârtie, microparticule $Fe/TiO_2$ (figura 3). Cantitatea de microparticule a fost introdusă în omogenizator, pentru dispersarea cât mai uniformă în pastă şi respectarea ordinii operaţiilor de preparare a pastei de hârtie. În figura 3 se ilustrează prezenţa şi distribuţia randomizată a microparticulelor de $Fe/TiO_2$, care se manifestă prin apariţia punctelor fluorescente (datorate materialului dopant) pe suprafaţa hârtiei, expusă acţiunii radiaţiilor ultraviolete cu lungimea de undă de 360 nm.

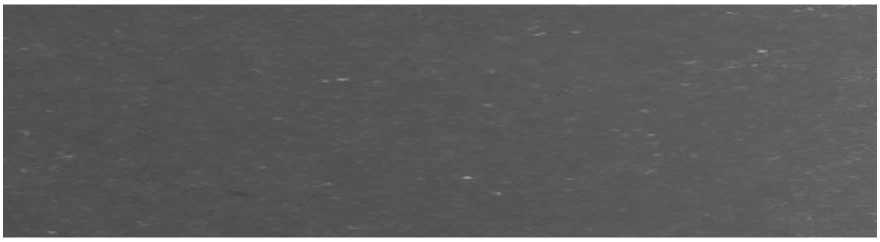

*Fig. 3 Distribuţia microparticulelor $Fe/TiO_2$ în foaia de hârtie*

### 3.2.1 Caracterizarea fizico-mecanică a foilor de laborator cu microparticule $Fe/TiO_2$

Valorile determinate pentru caracteristicile fizico-mecanice ale foilor de hârtie (tabelul 3) conduc la susţinerea următoarele afirmaţii:

*Tabelul 3 Caracteristicile fizico-mecanice ale foilor de hârtie obținute în laborator*

| Nr. crt. | Caracteristica | UM | Metoda de lucru | Rețeta martor | Rețeta Fe/$TiO_2$ |
|---|---|---|---|---|---|
| 1 | Gramaj | g/mp | SR EN ISO 536:2012 | 80,4 | 80,1 |
| 2 | Grosime | µm | SR EN ISO 534:2012 | 116 | 115 |
| 3 | Densitate aparentă | g/cm3 | SR EN ISO 534:2012 | 0,69 | 0,70 |
| 4 | Sarcina de rupere | N | SR EN ISO1924-2:2009 | 77,9 | 78,7 |
| 5 | Lungimea de rupere | m | SR EN ISO1924-2:2009 | 6.584 | 6.681 |
| 6 | Număr duble îndoiri | nr. | SR ISO 5626:1996 | 894 | 924 |
| 7 | Rezistența la plesnire | kPa | SR ISO 2758:2004 | 387 | 390 |
| 8 | Rezistența la sfâşiere | mN | SR EN ISO 1974: 2012 | 610 | 630 |
| 9 | Porozitatea Gurley, F/S | s | ISO 5636-5: 2003 | 60/57 | 62/59 |
| 10 | Conținut de cenuşă | % | SR ISO 2144:1999 | 9,64 | 9,65 |

- adaosul de microparticule în compoziția foilor de laborator nu modifică semnificativ grosimea şi densitatea acestora. De asemenea, microparticulele cu dimensiuni mai mici decât a fibrelor celulozice, nu contribuie la deformarea construcției matricei celulozice. Această constatare este susținută şi de rezultatele obținute la determinările de porozitate care oscilează foarte aproape de valorile constatate la proba martor.
- tot din aceleaşi motive (neafectarea structurii fibroase celulozice), nu s-au observat diferențe semnificative nici în cazul caracteristicilor de rezistență – lungimea de rupere, număr de duble îndoiri, sfâşiere sau plesnire.

Prin urmare, rezultatele prezentate în tabelul 3 arată că adaosul de microparticule folosit, 0,2g/kg hârtie, nu are o influență semnificativă asupra principalelor caracteristici fizico-mecanice ale foilor de laborator.

### 3.2.2. Caracterizarea magnetică a foilor de laborator

Studiul proprietăților magnetice evidențiază prezența dopantului (Fe - 0,9; 1,2; 5%), în structura $TiO_2$ şi are ca rezultat utilizarea în procesul de securizare a hârtiei. Probele preliminare evidențiază prezența magnetizației masice în foile de laborator cu adaos de 0,2g/kg hârtie.

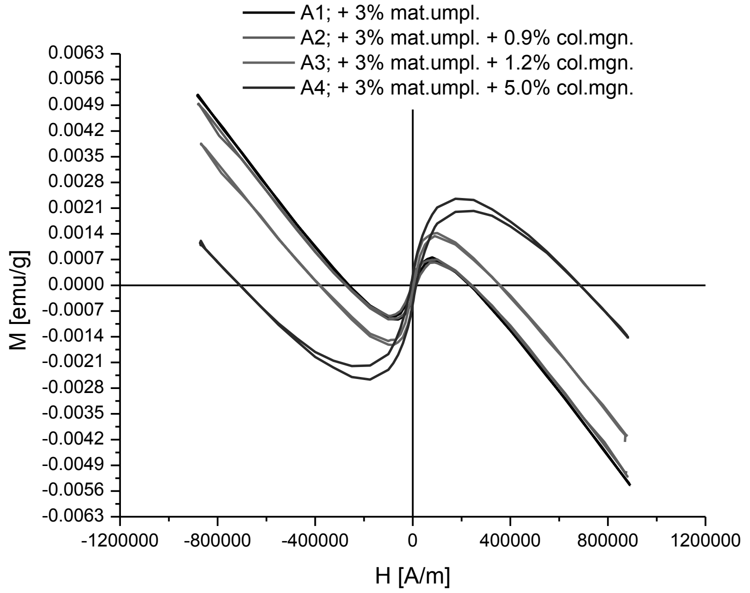

*Fig. 4 Curbe magnetizație remanentă: A1 – probă martor; A2 – Fe/$TiO_2$ - 0,9%; A3 - Fe/$TiO_2$ – 1,2%; A4 – Fe/$TiO_2$ – 5%.*

În figura 4 sunt prezentate curbele de magnetizare masică (emu/g hârtie) funcţie de câmpul magnetic aplicat (A/m) pentru probele de hârtie cu microparticule de Fe/$TiO_2$ (A1-A4). Magnetizaţia masică prezintă o creştere proporţională cu creşterea concentraţiei de Fe, de la 0,0009 emu/g hârtie pentru o concentraţie de 0,9% şi 0,0017 emu/g hârtie pentru o concentraţie de 1,2% până la 0,0027emu/g hârtie pentru o concentraţie de 5%. Existenţa magnetizării masice indică prezenţa unui material feromagnetic în structura probelor de hârtie, cel mai probabil fier [12].

Având în vedere valorile crescătoare şi precizia aparatului de măsură, precum şi adaosul destul de mic în foaia de hârtie (200g/t de hârtie – microparticule Fe/$TiO_2$), se poate considera că fenomenul feromagnetic este prezent în hârtie. Aşadar, rezultatele măsurătorilor demonstrează că:

- se poate mări adaosul de microparticule Fe/$TiO_2$- 0,9%, în masa hîrtiei pînă la obţinerea magnetizaţiei remanente dorite, fără ca hârtia să îşi modifice gradul de alb;
- în acelaşi timp se impune stabilirea randamentului de retenţie a amestecului celuloză/microparticule Fe/$TiO_2$.

## IV. CONCLUZII

1. Oxizii magnetici pe bază de $TiO_2$ dopat cu Fe au primit un mare interes în securizarea hârtiei datorită proprietăţilor feromagnetice. Originea feromagnetismului este puternic dependentă de concentraţia şi distribuţia dopajului.
2. Microparticulele de tip Fe/$TiO_2$ au fost obţinute relativ uşor prin combinarea metodelor umede coprecipitare şi hidrotermală.
3. Condiţiile optime de sinteză au fost: 0,9% - 5% gr. cantitate de element dopant, temperatura de calcinare 450$^0$C şi timp de calcinare 4h. În comparaţie cu metoda sol-gel, în procesul de sinteză utilizat se folosesc materii prime ieftine şi nu este necesară apelarea la solvenţi organici. De aceea, combinarea metodelor umede coprecipitare / hidrotermală reprezintă o alternativă pentru realizarea la scară pilot a microparticulelor Fe/$TiO_2$.
4. În urma analizelor efectuate s-a confirmat prezenţa dopantului în structura dioxidului de titan, mărimea particulelor de tip nano, precum şi proprietăţile feromagnetice.
5. Rezultatele experimentărilor preliminare demonstrează că hârtia poate fi securizată cu microparticule de tip Fe/ $TiO_2$, urmând ca problemele care au apărut pe parcursul desfăşurării cercetării să fie rezolvate în cadrul experimentărilor viitoare.
6. Susţinerea unui sistem integrat de securitate a hîrtiei presupune descoperirea sistemelor de detecţie magnetică potrivite. Acestea sunt destinate identificării contrafacerilor în domeniul documentelor de valoare. Acurateţea sistemelor depinde de utilizarea dispozitivelor mici, sensibile din punct de vedere magnetic, capabile să valideze microparticulele Fe/$TiO_2$ şi construite special pentru acestea.

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## BOOK REVIEW

# LIGNOCELLULOSE BIOREFINERIES

**Jean-Luc Wertz and Olivier Bedue, EPFL Press, 2013, 527 pp., ISBN 978-2-940222-68-1 (PFL Press); ISBN 978-1-4665-7306-2 (CRC Press)**

It is known that biomass represents a renewable resource assured by the biosynthesis process. According to the definition, biomass is any organic matter that is available on a renewable basis, including dedicated energy crops and tree, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other materials. Due to its composition, from biomass we can obtain, by complex processing, almost all chemicals resulted from petrochemistry. That is why, considering the exhausting fossil resources, it is expected that in the future biomass will satisfy all our needs. This comprehensive book covers practically all aspects, from the possibilities to increase the accessibility of raw materials to their conversion to different chemicals and energy sources.

In chapter 1 – **Introduction** – a review is presented concerning aspects of climate change (the earth's energy budget and greenhouse effect, carbon cycle), biomass and its conversion to products, biorefineries and the life cycle assessment, which are connected with the structure of the book.

In chapter 2 – **Photosynthesis, the ultimate beginning for biorefineries** – the elements involved in photosynthesis are analyzed (chloroplasts, photosynthetic pigments and antenna complexes), along with the stage of photosynthesis (light reactions and dark reactions) with examples of efficiency of the process in the case of different plants.

Chapter 3 is dedicated to the **Futures of first generation biorefineries**. In this context, the possibilities to use sugar, starch and vegetable oil feedstocks are known. By using these raw materials, it was possible to obtain the first generation of biofuels (bioethanol, ethyl tert-butyl ether), biodiesel, biogas and other liquid biofuels. At the same time, some examples of biobased chemicals and materials from food plant are mentioned. To develop industrial production, the important aspects of life cycle assessment and sustainability are considered.

As mentioned above, biomass processing has to be discussed from the composition viewpoint. Therefore, in the following chapters the main structural components of biomass are presented, along with their biological and chemical stability.

Thus in chapter 4 – **Cellulose, the predominant constituent of biomass** – information concerning the structure (at the molecular, supramolecular and morphological levels), biosynthesis (enzymatic polymerization of glucose in bacteria and plants), properties (mechanical and physical) and applications (in paper and man-made fibers production), is offered.

Chapter 5 – **Enzymatic and non-biological degradation of cellulose** – demonstrates that the structural complexity of cellulose represents a major problem in its degradation to obtain precursors, which can be used in obtaining biofuels and chemicals. The enzymatic degradation could be applied on a large scale by improving biochemical systems to access and hydrolyze cellulose, yields in the fermentation steps and optimization of biomass pretreatment conditions. The biodegradation of cellulose can be carried out using enzymes produced by bacteria and fungi to convert the insoluble substrate to soluble sugars. Therefore, important subjects are represented by producing cellulases and understanding the mechanisms of cellulose degradation. In this chapter, detailed information is provided on the composition of the enzymatic complex for different microorganisms (fungi and bacteria), mechanism, kinetic and activity. Despite its chemical stability, cellulose can be degraded non-enzymatically by acids, oxidants, thermal energy, mechanical means and radiation. From the large amount of information existing in this field, the authors retained the main aspects concerning the mechanism and products that can be obtained following degradation, and underline the physical and chemical ways in biomass pretreatment.

**Hemicelluloses and lignin, other key constituents of biomass** are presented in chapter 6. Hemicelluloses represent one of the three major components of biomass and are present under various forms in all green plants. The structure and occurrence, biosynthesis, their role in the cell wall, properties and applications are described in this chapter. Lignin is a complex phenolic polymer that imparts strength, rigidity and hydrophobicity to plant secondary cell walls. The structure and distribution of lignin are analyzed along with its biosynthesis process and the interaction with other components of the cell wall. Although lignin is extremely recalcitrant to degradation, this process is possible by the action of basidiomycetes white-rot fungi, which are able to degrade lignin efficiently using a combination of extracellular lignolytic enzymes, organic acids, mediators and accessory enzymes. This process is described in detail with a presentation of the enzymes that are involved in the degradation of lignin. At the same time, it is mentioned that lignin can represent a polymer with both low- and high-value applications, which are expected to become enormous over the upcoming decades. Many structural and compositional factors hinder the enzymatic digestibility of cellulose present in lignocellulosic biomass.

That is why, pretreatments are necessary, as presented in chapter 7 – **Pretreatments of lignocellulosic biomass**. The goal of any pretreatment is to alter the structure of the lignocellulosic materials to make cellulose and hemicelluloses more accessible to the enzymes that convert polysaccharides into fermentable sugars. The pretreatment methods can be divided in the following categories: physical pretreatments of biomass involving milling and high-energy radiation, chemical methods involving liquid hot water, dilute and concentrated acids, alkali, organic solvent, oxidizing agents and ionic liquids, physico-chemical methods involving steam explosion, ammonia pretreatments, $CO_2$ explosion, mechanical/alkaline pretreatments and biological methods. As a conclusion, the authors summarize that biomass pretreatment remains the bottleneck in the processing of lignocellulosics for biofuels and other biobased products. Although some pretreatment methods show apparent advantages, it is unlikely that one method will become the method of choice for the diversity of biomass feedstocks, which can react differently to a given technology.
Lignocellulosic biomass feedstock can be converted to biofuels and chemicals through multiple processes. Conversion technologies fall into two main categories: biochemical conversion and thermochemical conversion.

**Biochemical conversion of biomass** represents the subject of chapter 8. The main steps of this process are represented by pretreatment, hydrolysis and fermentation. Pretreatment can fractionate the cellulose, hemicelluloses and lignin components. For carrying out hydrolysis and fermentation, there are different strategies including separate enzymatic hydrolysis and fermentation, simultaneous saccharification and fermentation, simultaneous sachharification and co-fermentation and consolidated bioprocessing. Along with ethanol, fermentation allows obtaining lactic and succinic acids, important precursors for other bioproducts. In this chapter, the life cycle assessments are discussed and the results obtained by different companies at different levels are presented, including not only ethanol, but also other chemicals. The chapter also offers some examples concerning lignin uses, which can significantly increase the competitiveness of cellulosic ethanol technology.

The thermochemical platform for conversion of lignocellulosic biomass aims to efficiently produce biofuels and chemicals via processes that use heat and chemistry (chapter 9 – **Thermochemical conversion of lignocellulosic biomass**). Primary routes for biomass thermal conversion are the following: combustion, gasification and pyrolysis. Different variants are analyzed, along with life cycle assessments. At the same time, in this chapter case studies are presented and some information concerning the technology used, products and technology scale is systematized.

The last chapter is dedicated to **Perspectives**. It is mentioned that the biorefineries were identified as a potential solution to mitigate the threat of climate change and to meet the growing demand for energy and non-energy products. The comparison between first generation and second generation biorefineries, which generated the “food versus fuel” debate, demonstrates that the latter variant, which involves the use of lignocellulosic feedstocks, such as organic wastes and residues, and their conversion into energy and chemicals, has multiple advantages. At present, there are representative programs both in the USA and EU stimulating the improving of both feedstock yield and composition of biomass (plant genomics, breeding programs and the chemical engineering of desirable traits – drought resistance, photo-cycle intensity, cold tolerance, sugar composition C5/C6) and processes (biochemical platform and thermochemical platform). Developing these technologies can allow obtaining fuels and chemicals according to the principles of sustainability.

This book represents a valuable instrument to serve as a reference for policy makers, industry leaders, professors, teachers, scientists, engineers and students who are involved in promoting the bioeconomy.

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