**Journal of Physical and Theoretical Chemistry**
of Islamic Azad University of Iran, 4 (3) 155-161**:** Fall 2007
(J.Phys.Theor.Chem.IAU Iran: Fall 2007)
ISSN: 1735-2126

# Deinking of Laser Printed Copy Paper by Chemical Different Treatments and Effect on Optical and Strength Properties of Paper

A.A.Salari[1*] , M. Ghasemi Kochameshgi[1] and A. Aminifar[1]

1. Department of Chemistry, Shar-e-rey Branch, Islamic Azad University, Shar-e-rey, Iran

## ABSTRACT

Paper recycling in an increasingly environmentally conscious world is gaining importance. With rapid developments in deinking processes for the reuse of secondary fibers being made, the recycling process is become more and more efficient. This work investigated the effect of chemical different treatments including $H_2O_2$ and NaOH on repulping and flotation operations during the deinking of laser printed copy paper, and freeness and physical properties of handsheets were evaluated. In order to access to more desirable quality specification and strength properties in paper production recovered from primary materials, NaOH and $H_2O_2$ , as an effective factor in recovery, were added to the pulp of printer waste paper in a different ratio. Results of this research show that, the optimum rate of handsheet paper was in freeness 300-400 ml, which this rate, have better effect. In optical and mechanical properties of handsheet papers, maximum and minimum rate were 2 to 3 (C) and 1 to 2 (A) percent ratio of NaOH to $H_2O_2$ respectively.

**Keywords:** Recycling; Deinking; Handsheet; Freeness; Flotation

## INTRODUCTION

The collection and removal of hydrophobic particles by air bubbles from the pulp slurry, i.e. flotation, is described by the well known first order equation [1,2].

$$\frac{d_{N_p}}{d_t} = -Z_{pb} P_c P_a P_s \qquad (1)$$

where *N*p is the particle number concentration, *P*c, *P*a and *P*s are the probabilities of particle-bubble collision, attachment and stabilization, and *Z*pb is the particle-bubble collision rate in a turbulent flow which, in low turbulent dissipation regions, is given by Ref.[3].

$$Z_{pb} = N_p N_b \sqrt{\frac{8\pi E_T}{15\nu}} \left(\frac{d_p + d_b}{2}\right)^3 \qquad (2)$$

$E_T$ is the turbulent dissipation rate per unit mass, $\nu$ the kinematic viscosity and *N*p, *N*b and *d*p, *d*b are the particle and bubble number concentration and diameter, respectively[4].

Recycled waste paper has become an important and environmentally benign source for new fibers for papermaking. However, in the last few years there has been a substantial increase in the portion of difficult-to-deink xerographic and laser printed papers [5].

Thus, recycling of the waste papers must be considered, as an economic necessity. Recycled waste papers have become an important source of new fibers in paper making throughout the world. Office waste papers which consist mainly of laser printed and xerographic papers, form a fast growing source for paper recycling due to the increase in the utilization of office photocopiers and computer printouts. The reuse of these waste papers is limited because the ink formulation used in these papers are difficult to be removed by conventional techniques such as dewashing, dispersion, washing and flotation. Moreover, most of the conventional chemical deinking techniques require the use of large amount of chemicals such as sodium carbonate, sodium hydroxide, sodium silicate, hydrogen peroxide, hypochlorite, chelating agents and surfactants [6,7,8,9].

The molecular diffusion of surfactants is well described by the diffusion equation (Fick's law).

$$\frac{\partial c}{\partial t} = D\nabla^2 c \qquad (3)$$

Where $c$ is the surfactant concentration, $D$ is the molecular diffusivity, $t$ is the reference time and $\nabla^2$ is the Laplace operator.

For a planar gas–liquid interface, the partial differential Eq. (3) reduces to a one-dimensional case, which can be analytically solved. In terms of the dynamic surface excess, Γ(t), of the adsorbed surfactant molecules, the solution of the one-dimensional diffusion equation can be used to obtain the celebrated Ward and Tordai (1946) expression, which is widely used in the modelling of the dynamic surface tension [10, 11,12].

The celebrated Ward and Tordai equation gives

$$\Gamma(t) = \sqrt{\frac{D}{\pi}}\left[2c_b\sqrt{t} - \int_0^t \frac{\phi(t)}{\sqrt{t-\tau}}\,d\tau\right] \qquad (4)$$

Where $c_b$ is the surfactant concentration in the bulk solution, $\phi(t)$ is the surfactant concentration at the subsurface layer and τ is the integration variable.

The use of Eq. (4) for adsorption at planar surfaces in the modelling of the dynamic adsorption of surfactant molecules onto a flotation air bubble can be questioned since the gas–liquid interface is strongly curved [13].

It was previously noted that laser printed white copy papers are difficult to deink with conventional deinking methods [14,15]. The reduced efficiency is due primarily to the strong adherence of polymeric toner particles to the fiber surface. Recycling mills therefore use increasingly costly mechanical devices for breaking down the large, non-impact ink particles to facilitate removal by flotation or washing [14,16,17]. These intensive mechanical forces are energy demanding and shorten the fibers, decreasing the freeness and strength of the paper formed from these fibers. There would be significant benefit if an effective means were found to promote the release of toners from office waste [14].

It has been shown [18] that the distributed performance of a flotation bank can be properly characterized by the tanks-in-series model, Eq. (5), considering a rectangular rate constant distribution function to account for the rate constant change along the bank, while keeping a constant residence time for each cell.

$$R = R_{Max}\left[1 - \frac{(1-(1+k_{Max}\tau)^{1-N})}{(N-1)k_{Max}\tau}\right] \qquad (5)$$

Where R is the cumulative mineral recovery in the flotation bank, $R_{MAX}$ is the maximum recovery at infinite time, $k_{MAX}$ is the maximum rate constant of the rectangular distribution function, τ is the residence time of one cell and N is the number of cells in the bank. Eq. (6) is only useful for N > 1. For N = 1, the solution is given by the following equation.

$$R = R_{Max}\left[1 - \left(\frac{\ln(k_{Max}\tau + 1)}{k_{Max}\tau}\right)\right] \qquad (6)$$

Also, a flotation bank simulator, based on the same model, can be used in order to account for changes in pulp flowrate along the flotation bank, as well as the corresponding change in cells pulp residence time [19].

Paper recycling industry have been propounded as a need due to some economical and environmental reasons including; lack for initial fiber material, incremental demand for cellulosic products such as paper by human society, environmental problems as a result of deforestation, incremental cost of producing paper and cardboard from raw cellulosic material as well as high cost of energy. All mentioned reasons cause recycling of used products to be an acceptable strategy in all around the world and it is pursued seriously though applied and scientific research. Iran is one of the country that import various kind of paper products about 800,000 ton each year and there is a growing demand on it, as can be found out paper recycling have an important contribution to economy [20].

# MATERIAL AND MEDTHODS

## 1. Sampling

In this study, we aimed recycling of printing wastepaper to produce recycled paper. We used printing wastepaper from COPIMAX Company that had been become as wastepaper because of different reasons mainly editorial reasons after printing and print just on one side of them. That paper transformed into smaller ones and transferee in a plastic bag and kept for 24 in the laboratory.

In order to eliminate ink from wastepaper, we used flotation as deinking method. Deinking step can be divided into three stages as follow:

1- Repulping
2- deinking (removal of ink from pulp)
3- washing

## 2. Repulping procedures

The first step in recycling of paper is the repulping at which wastepaper are converted in to the paper pulp. It should be considered that distance between physical properties of pollutant and those of dispersed fibers must be large. An accurately weighted amount of dry wastepaper about 25 gr was defiberd in which fibers of wastepaper separated from each other to defibration appropriate amount of water mixed with paper in a initial pulper that contains plastic vane flexible for separation of moist fibers at the suitable angle. This process was done at the temperature $60^{\circ C}$-$70^{\circ C}$ for 30 or 45 minutes. A blender was used to separate fibers completely for about 30-60 seconds. In this step, printed tuner on the paper converted into very small (tiny) granules, therefore tiny granules or suspended ink in suspension either separate from each or adhere to fiber.

Chemical materials such as sodium hydroxide, sodium silicate, hydrogen peroxide, detergent contain lipase and cellulose weighted and added to paper pulp. The content was mixed well in a mixer with plastic vane for about 5-25 minutes. In order to investigation of chemical material on bond between ink fiber, the mixing process was done at $50^{\circ c}$ a warm water bath was used to control and to fix the temperature of suspension of pulp.

Chemical material was used as follow:

1- sodium hydroxide (NaOH) 2%, 3% in proportion to weight of dry wastepaper (variable parameter)
2- hydrogen peroxide ($H_2O_2$) 1% , 2% , 3% in proportion to weight of dry wastepaper (variable parameter)
3- sodium silicate ($Na_2SiO_3$) 3% in proportion to weight of dry wastepaper

## 3. Flotation procedures

As mentioned earlier, flotation method was used to remove ink from wastepaper pulp. In our study, produced pulp was transferred into a flotation cell which is made from PVC materials and equipped with two concenter pipe with some aperture on the inner pipe to pulp slurry.

Chemical material used in deinking step, were as follows:

1- fatty acids (soap) 0.5 % - 1 % in proportion to weight of dry wastepaper.
2- detergent contain lipase and cellulose, 2 % in proportion to weight of dry wastepaper.
3- Calcium chloride 1% in proportion to weight of dry wastepaper.

Physical parameters in this step are temperature and time of flotation process of ink that were taken 40 $^{\circ C}$ and 20 min, respectively. We collected generated foam on the surface of flotation cell manually and continuously, indeed foams were mix of fiber and ink particles, then removed from system. After finishing this step, aeration was stopped and deinked pulp were collected.

## 4. Washing

We used a sieve with 200 to mash the deinked pulp. This step is necessary to clean the deinked pulp and to reduce amount of existence printing tuner in the pulp paper that weren't separated in flotation step.

Experimental condition and amount of used chemical materials in repulping and flotation steps are shown in table 1.

**Table 1.** Repulping and flotation operation conditions

| Step | Repulping | Flotation |
|---|---|---|
| Time (Minutes) | 30 or 45 | 15 |
| Temperature (º C) | 60 - 70 | 40 |
| NaOH | 2% and 3% | - |
| $H_2O_2$ | 1% and 2% and 3% | - |
| $Na_2SiO_3$ | 3% | - |
| EDTA | 0.5% | - |
| Surfactant | - | 0.5% or 1% |
| Detergent (lipase, cellulose) | - | 2% |
| Time(Minutes) | - | 15 |
| Temperature (º C) | - | 40 |
| pH | 10 or 11 | 10 or 11 |

**Table 2**. Various ratios of NaOH and $H_2O_2$

| sample | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| $H_2O_2$ | 1% | 2% | 3% | 1% | 2% | 3% |
| NaOH | 2% | 2% | 2% | 3% | 3% | 3% |

With regard to data in table 1,various proportion of soda and hydrogen peroxide were used and results are summarized in table 2, (number of component denote various ratios of NaOH and $H_2O_2$). Six types of handsheets according to applied mixing proportions and totally sixty papers were made.

**5. Handsheet preparation**

Sample handsheets were manufactured according to TAPPI standard number T205 om-88. If there is a need for disintegration of pulp, which means dispersion of pulp sample or initial matter in making paper in order to obtain a suspension of free fibers, fibers separated well from each other using a disintegrator instrument with 1000 round per minute (rpm) speed. Then fiber solution was prepared with appropriate fluidity degree and dryness percentage 3%. Finally certain amount of pulp paper (400ml), considering initial weight of paper that was 60 gr. per square meter in our work, was used to manufacture paper.

**6. Physical properties**

Measurement of physical and optical properties was conducted after flotation. Pulp freeness was determined according to TAPPI standard T 227 om – 92. Physical testing (Burst, Tensile , Tear) and brightness, opacity of the handsheets was done following TAPPI standard T 403 om- 97 and TAPPI standard T 452 om-92 (Brightness of pulp paper and paper board), respectively.

## RESULTS AND DISCUSSION

**1. Freeness and physical properties of handsheets**

Pulp freeness was measured for each treatment after the flotation process (Table 3).

Physical properties and freeness each of handsheet samples (that made up according to table 2), are shown in table3. The results indicated that, inspite of, samples have alike grammage, bulk variation depend on variation of density and thickness of paper, so that with increasing of bulk, the density was decreased and thickness of paper was increased. In samples of C and F freeness had minimum rate, that were 384 and 334 mm, respectively. In samples (C, F), density was maximum rate and hence, bulk was decreased. Results of this research show that, the optimum rate of handsheet paper was in freeness of 300-400 ml.

**2. Brightness**

The brightness of all handsheets produced using the six deinking process was measured and compared with each other (Fig.1) The data

**Table 3**. Physical properties and freeness of each handsheet samples

| Sample | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| Grammage ($gr/m^2$) | 59 | 60 | 62.5 | 60.8 | 61.4 | 61.7 |
| Freeness (ml) | 472 | 490 | 384 | 436 | 413 | 344 |
| Density ($gr/cm^3$) | 0.598 | 0.606 | 0.622 | 0.602 | 0.610 | 0.617 |
| Bulk ($cm^3/gr$) | 1.672 | 1.650 | 1.608 | 1.661 | 1.639 | 1.621 |

shown that, The maximum and minimum rates of brightness were in 3 to 2 ratio (C) and 1 to 2 (A) of $H_2O_2$ to NaOH, respectively (Table 2).

Statistical analysis of variables was performed using one way ANOVA Analysis based on the SPSS version 14 software at the confidence level of 95% that, there were significant difference between of treatments ($p<0.05$). In other words, with increasing of $H_2O_2$ rates, the brightness of paper was increased, because $H_2O_2$ prevent from to turn yellow or to darken by NaOH on pulp. Moreover ink separation, it helps to primary whiteness in step of deinking.

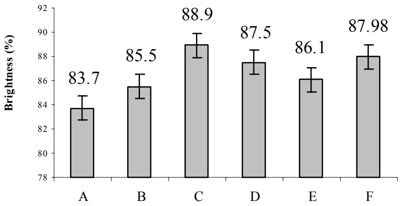


**Fig.1.** Brightness of various samples after deinking (different ratios of $H_2O_2$ and NaOH according to table2)

## 3. Opacity

The results from opacity experiments of handsheets was shown in Fig.2 Maximum and minimum rate of opacity in 3 to 3 (F) and 1 to 1 (A) of $H_2O_2$ to NaOH (Table 2) respectively. There are many factors that effected in opacity, including: grammage and fillers. The increasing of opacity rates of hand sheets, depend on kinds of fillers in chemical waste paper, that they form 40 percent of paper weight. Fillers increase the light-scattering coefficient, and consequently cause increasing of opacity paper. In addition to, fillers decrease the expenses of produce economically.

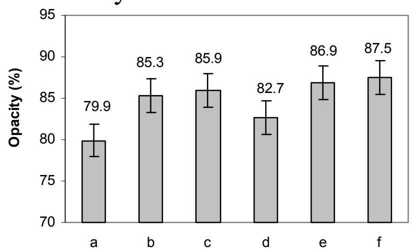


**Fig.2.** Opacity of various handsheets after deinking.

## 4. Mechanical properties of handsheets

The effect of various deinking treatments on the strength properties of pulp was studied, and the results of burst index, tensile index and tear index are illustrated in Figs. 3-5.

The rates of resistance to burst index of handsheets are shown in Fig.3 Maximum and minimum rates of resistance to burst were in 3 to 2 ratio and (C) and 1 to 2 ratio (A) of $H_2O_2$ to NaOH (Table 2) respectively. Comparisons of means ($\alpha$ 5%) between different ratios illustrated that, there is not significant difference between F and C. The rates of resistance of paper depend on rates of bounds between fibers. If fibers was thinner or flexibility, firmness of bounds between fibers had been increased, because hydrogen connections between fiber increase and so resistance of paper in front of burst increase.

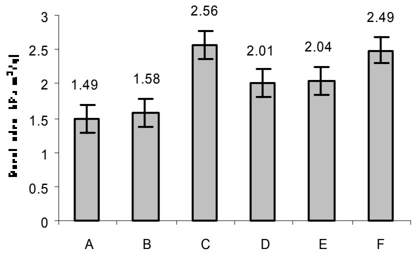


**Fig.3.** Burst strength of various samples after deinking (different ratios of $H_2O_2$ and NaOH according to table 2)

Tensile index of hand sheets are shown in Fig.4 Maximum and minimum rates of tear were in 3 to 2 ratio and (C) and 1 to 2 ratio (A) of $H_2O_2$ to NaOH (Table 2) respectively. The rate of tear index depend on increasing of bounds between fibers. In other words, if the connection between fibers was more, the rates of tensile had increased, too. Analysis of data indicated that, there is a significant difference between treatments. But, there is not significant difference between ratios of F and E.

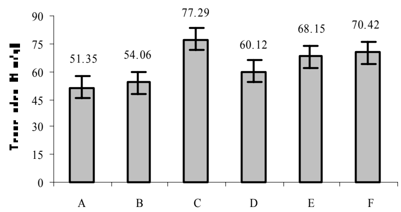


**Fig.4.** Tensile strength of various samples after deinking (different ratios of $H_2O_2$ and NaOH according to table 2)

Tear index of handsheets are showed in Fig.5 Maximum and minimum rates of tear were in 3 to 3 ratio and (B) and 2 to 2 ratio (F) of $H_2O_2$ to Na OH (Table 2), respectively. The analysis of data indicated that, there is a significant difference between treatments. But, there is not significant difference between ratios of C and F ratios.

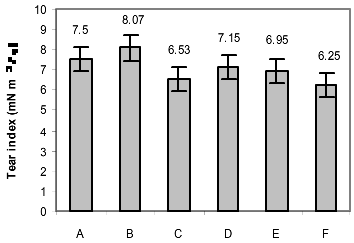


**Fig.5.** Tear strength of various samples after deinking (different ratios of $H_2O_2$ and NaOH according to table2)

## REFERENCES

1. N.Ahmed, G.J. Jameson, Flotation kinetics, Miner. Process. Extract. Metallur. Rev.5 (1989) 77–99.
2. F. Julien Saint Amand, Hydrodynamics of deinking flotation, Int. J. Miner. Process 56 (1999) 277–316.
3. P.T.L.Koh, M.P. Schwarz, CFD modelling of bubble-particle collision rates and efficiencies in a flotation cell, Miner. Eng. 16 (2003) 1055–1059.
4. Beneventi,D. Benesse,M. Carre,B. Julien Saint Amand,F. Salgueiro,L. (2006) Modelling deinking selectivity in multistage flotation systems. Separation and Purification Technology (2006) 1-11.
5. Gubitz, G. M., Mansfield, S. D., Bohm, D and Saddler, J. N. 1998. Effect of endoglucanases and hemicellulases in magnetic and flotation deinking of xerographic and laser-printed papers. Journal of Biotechnology, 65: 209-215.
6. Lee, C. K., Darah, I. and Ibrahim, C. O. 2007. Enzymatic deinking of laser printed office waste papers: some governing
7. parameters on deinking efficiency. Bioresource Technology, 98: 1648-1689.
8. Marques, S., Pala, H., Alves, L., Amaral-Collaco, M.T., Gama, F.M., Girio, F.M., 2003. Characterization and application of glycanases secreted by *Aspergillus terreus* CCMI 498 and *Trichoderma viride* CCMI 84 for enzymatic deinking of mixed office waste papers. J. Biotechnol. 100, 200–219.
9. Prasad, D.Y., Heitman, J.A., Joyce, T.W., 1993. Enzymatic deinking of colored offset newsprint. Nordic Pulp Paper Res. J. 2, 284–286.
10. Woodward, J.L., Stephan, M., Koran, L.J., Saddler, J.N., 1994. Enzymatic separation of high quality unlinked pulp fibers from recycled newspaper. Biotechnology 12,905– 908.
11. Ward, A.F.H., Tordai, L., 1946. Time-dependence of boundary tensions of solutions: I. The role of diffusion in time effects. The Journal of Chemical Physics 14 (7), 453–461.
12. Chang, C.H., Franses, E.I., 1995. Adsorption dynamics of surfactants at air/water interface: a critical review of mathematical models, data and mechanisms. Colloids And Surfaces. A, Physicochemical And Engineering Aspects 100, 1 –45.
13. Eastoe, J., Dalton, J.S., 2000. Dynamic surface tension and adsorption mechanisms of surfactants at the air–water interface. Advances in Colloid and Interface Science 85, 103– 144.
14. Nguyen,V,Anh. Phan,M,Chi. Evans,M,Geoffrey (2006). Effect of bubble size on the dynamice adsorpation of frothers and collectors in flotation.Int. J. Miner. Process.79 (2006) 18-26.
15. Qian, Y. and Goodell, B. 2005. Deinking of laser printed copy paper with a mediated free radical system. Bioresource Technology, 96: 913-920.
16. Vidotti, R.M., Johnson, D.A., Thompspn, E.V., 1992 Pulping conference proceedings. TAPPI PRESS. Atlanta, p.643.
17. Quick, T. H., Hodgson, K. T., 1986. Xerography deinking – a fundamental approach.Tappi j. 69 (3), 102-106.
18. McBride, D., 1994. High- density kneading system offers alternative to conventional

deinking. In: Advances in Paper Recycling. Miller Freeman Books, New york.

19. Corte´s, F.L., Yianatos, J.B., Urtubia, H.C., 1995. Characterization of the copper-moly collective flotation circuit at Divisio´n Andina, Codelco- Chile. In: Casali, A., Dobby, G., Molina, M., Thoburn, W. (Eds.), Copper'95, Mineral Processing and Environment, vol. II. IIMCh-CIM-AIME, Santiago, Chile, pp. 37–51.
20. Yianatos,J,B. Henriquez,F,D. (2006). Short – cut method for flotation rates modeling of industrial flotation banks. Minerals Engineering 19 (2006) 1336-1340.
21. Talayipoure, M., Resalati, H., and Mirshokraei, S. A.2003.Recycling of chemical printing waste paper and effect of mixture its with CMP pulp for producing of printing paper. The First Congress on Cellulousic Processing and Utilizations, University of Tehran, 355-372.