

IMPROVED PERFORMANCE TMP BLEACHING CHEMICALS FOR CLOSED MILL SYSTEMS

Part. 1: Metal management and bleaching chemistry

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KEY WORDS

Zeolite, impregnation, chelation, stabilization, bleach effluent, peroxides thermomechanical pulp.

ABSTRACT

The performance of bleaching chemicals impregnated on a zeolite support has been evaluated in pulp pretreatment and bleaching processes. Citric-, pyromellitic- and diethylene triaminepentamethylene phosphonic- acids were separately supported on a Na-A zeolite. These zeolite-supported chemicals were then used as pretreatment and stabilizing agents during peroxide bleaching of TMP. A significant decrease in the heavy metal content in pulp was achieved by pretreating TMP with porous zeolite supports of citric acid and pyromellitic acid. Zeolite-supported citric acid and zeolite-supported pyromellitic acid systems showed synergistic chelation effects over the separate addition of citric acid, pyromellitic acid and zeolite alone. Metal chelation was most effective between pH 4 and 6. Increasing pretreatment temperature above 50 °C also improved heavy metal chelation. Excellent peroxide bleach stabilization resulting in a significant drop in peroxide consumption was obtained by adding a zeolite support of polyamino phosphonic acid in the bleach liquor. The other advantages of zeolite support chemicals were slower accumulations of dissolved solid in recycled white water and good recycling efficacy of bleach effluent.

INTRODUCTION

Decomposition of hydrogen peroxide is one of the major causes for a loss of bleaching efficiency of mechanical and thermomechanical pulps. The readily soluble hemicelluloses also produce a high effluent load, if mechanical pulp is treated with bleaching agents under an alkaline condition. It is also stated in literature [1] that an alkaline process would result in too many dissolved organic compounds in the water circuit. High amounts of total dissolved solid (TDS) are considered to be an enemy for a closed-loop cycle because even after treatment, the effluent will still contain higher levels of most contaminants including solids, organics, and ionic species [2,3]. Minimization of dissolved solids including organics and ionic species in recycled white water is one of the priority research areas in the papermaking process.

DTPA is an effective heavy metal chelant under slightly acidic condition but chelation efficiency decreases with increasing alkalinity [4]. Moreover, the use of DTPA and other chelating agents need to be restricted due to their ecological impact [5]. Zeolite is a known ion-exchanging agent for hard water treatment. Again, zeolite is one of the most commercially used catalytic supports for oxidative, reductive reactions as well as for oxidative bleaching of textile [6]. Recently, we have demonstrated that zeolite can be used as a catalytic support for deinked pulp bleaching [7]. For these reasons, a combination of organic acid chelant with a porous, insoluble sodium alumino-silicate represents an interesting alternative. Pretreatment of wood pulp with a combination of zeolite A and organic acid such as citric acid or gluconic acid are reported to have a good stabilization effect on peroxide bleaching [8]. It is previously reported that zeolite can be used as a filler in mechanical pulp in order to increase fines retention, improve opacity of paper and reduce cost without any deterioration of mechanical properties [9]. These advantageous properties of zeolite prompted us to study the effect of this chemical in TMP brightening.

An alkaline solution of sodium silicate performs well as a bleach stabilizer though it can be a source of specific problems in downstream processes and in a close-loop cycle as well. Reportedly, a polyamino phosphonic acid salt, namely, DTPMPA, is one of the best peroxide stabilizer [10]. The later is also suitable substitute for alkaline Na-silicate in peroxide bleach stabilization [10]. Certain organic acids are efficient peroxide stabilizers. It is thought that effectiveness of these peroxide stabilizers can be improved by impregnating them on porous zeolite. Again, porous zeolite has strong adsorption capacity. Therefore, zeolite is expected to play an important role in controlling TDS content in spent water after bleaching.

This investigation summarizes the effects of various zeolite-support chemicals as pretreatment and stabilizing agents on bleaching efficiency. The specific objective of this report is to determine optimum composition of zeolite-support chemicals in pretreatment and bleaching stages. Especial emphasis is given on hydrogen peroxide consumption during bleaching reactions and the recycling performance of the effluent generated in the bleaching process. A comparison of the bleaching performance of zeolite-support chemicals with commercially used Na-silicate was also reported.

EXPERIMENTAL

Materials used

The following reagents and raw materials were used:

A thermomechanical pulp (70% Spruce/30% Balsam) from a Canadian paper mill; commercially available chelating agents such as diethylene triaminepentamethylene-phosphonic acid (DTPMPA), DTPA and citric acid; pyromellitic acid (1,2,4,5 benzene tetracarboxylic acid; sodium silicate (41 °Be); a commercially available detergent grade Na-A zeolite; commercial grade hydrogen peroxide (39.6% active).

Zeolite-supports of chelating agents and stabilizer were obtained by first mixing and impregnating industrial grade organic acids (citric, pyromellitic and polyamino phosphonic acid) on a commercially available Na-A zeolite in a tank prior to pulp treatment. The treatment process is inexpensive and simple. In a mill scale production, this treatment process can be performed in batch and mixing time is short (usually 5 min). Alternatively, it can be prepared and supplied from a separate industrial unit. Three zeolite supports used in this investigation were: polyamino phosphonic acid- zeolite support (Phos.Zeo) as stabilizer; citric acid- zeolite support (Na-cit.zeo) and pyromellitic acid- zeolite support (Na-pyromel.zeo); the later two are chelating agents.

Pretreatment

Using commercial citric acid and zeolite, the chelation parameters such as concentration, pH, reaction time and temperature were varied. Two zeolite-support systems were also tested for metal sequestration. All pretreatment were carried out at 3% pulp consistency. Initially, two and three factorial screening designs were used to determine suitable concentrations of pretreatment chemicals and preferred process condition such as pH, retention time and temperature. In a two-factorial screening design the preferred concentration range of chemical and preferred pretreatment temperature range had been determined. Chelant concentration was examined between 0 and 3 wt% and pretreatment temperature range was between 30 and 70 °C. Retention time and pH were maintained constant at 30 min and 5.5 respectively. Once the preferred concentration of each chemical and pretreatment temperature had been determined, classical experiments were carried out to study the effect of retention time. The effect of pretreatment time was examined for 5, 15, 30 and 60 min. Finally, a three-factorial screening design was carried out to determine the linear and interactive effects of time, temperature and pH on chelation efficiency. The chelation temperature was varied from 30 to 70 °C in steps of 10°C, chelation

time was maintained between 30 and 60 min in steps of 15 min and the pH range was 5 to 8.5 with an interval of 0.5 pH unit. For each statistical experiment variance and correlation factor have been calculated. Statistically significant interaction effects were also evaluated.

Iron, copper and manganese concentrations were determined twice by atomic absorption spectroscopy according to TAPPI Test Method T-266 om-94.

Bleaching trials

Screening tests were carried out to note the effect of various zeolite support chemicals on the bleach stabilization and peroxide brightening of TMP. The stabilizer concentration was varied between 1% and 5%. Bleaching conditions were then optimized using a 3-factorial Box Benkhen design. The design parameters in terms of coded variables are given in **Table 1**.

Table 1. Experimental design parameters for zeolite-support chemicals in bleaching

Factors	-1	0	+1	Step
H ₂ O ₂ , wt%	1	2	3	1
NaOH, wt%	0.5	1.25	2	0.75
Phos.Zeo, wt%	1	2.5	4	1.5

Bleaching trials were also carried out in duplicate with an alkaline solution of Na-silicate. The above experiments were performed in order to compare the peroxide bleach stabilization efficiency of Phos.Zeo with alkaline Na-silicate. Trials were performed at 10% pulp consistency for 2h at 70 °C. Two percent hydrogen peroxide was used for all experiments. For comparison purpose similar experiments were also carried out with polyamino phosphonic acid, e.g.

DTPMPA, as bleach stabilizer replacing Phos.Zeo or Na-silicate. Bleach liquor was sampled at the end of the run to measure residual peroxide, residual alkali and chemical oxygen demand (COD). Excess alkali was neutralized, and pH was adjusted to 5.5 with sodium metabisulfite. Handsheets were made according to TAPPI Test Method T 272 om-92. Brightness was measured in ISO scale according to CPPA standard method E1; CIE L*,a*,b* co-ordinates were measured according to CPPA standard method E5-P. The term bleaching efficiency used in this text can be expressed as $(\text{change in ISO brightness})/(\text{concentration of hydrogen peroxide consumed}) \times 100$. All concentration terms used in this investigation were expressed in percent of weight/weight of o.d. pulp.

Recycling of bleach effluent

The bleach effluent was diluted with fresh deionized water in 1:1 ratio. Diluted bleach effluent was then recycled back in the bleach liquor to carry out bleaching operation. After bleaching reaction, the brightness gain and the residual peroxide content in the bleach liquor were measured. The amount of total dissolved solid (TDS) in recycled bleach effluent was also reported. In another set of experiments the bleach effluent was clarified with 0.15% of a cationic polyacrylamide by dissolved air flotation (DAF) technique in our laboratory. The suspended solid and dissolved solid contents of the treated water were about 550 mg/L and 110 mg/L respectively. This treated bleach effluent was then used to prepare bleach liquor and the pulp brightening efficiency of this liquor was reported.

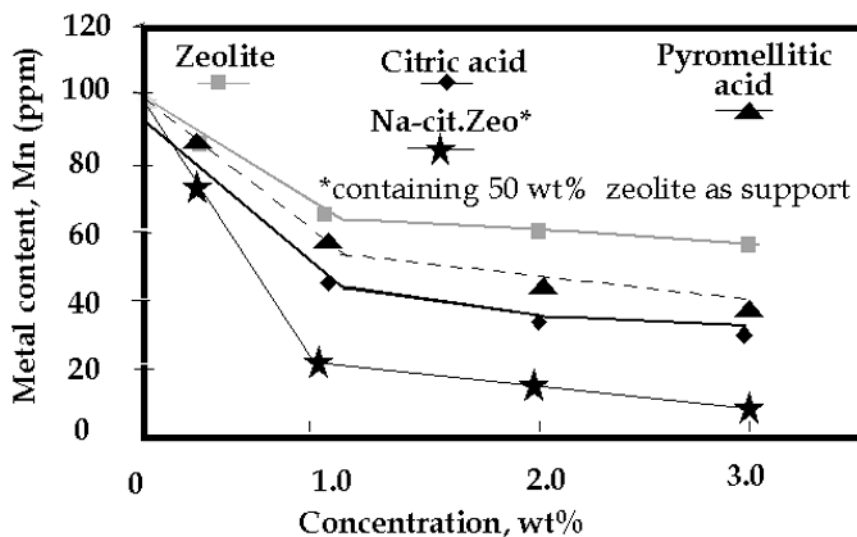
Results and discussion

Pretreatment

Simple washing of the pulp resulted in a decrease in Mn and Fe contents from 101 and 110 ppm to about 78 and 68 ppm respectively. The initial Cu

content in the pulp was 2.5 ppm and the change of Cu content after washing was negligible. We evaluated the chelation efficiency by comparing the heavy metal contents in pulp before and after the pretreatment and washing. We determined the metal contents for Mn, Fe and Cu in pulp. **Figure 1** presents the results of chelation of Mn with an unmodified zeolite, two organic acids and a zeolite-support chemical (Na-cit.zeo) as a function of their concentrations. Pretreatment conditions were 60°C and 15 min at pH 5.5. Increasing chelant concentration from 0 to 1% decreased the metal content fairly rapidly. Further increase in the chelant concentration to more than 1% had only a marginal effect on the pulp metal profile. Separate addition of citric acid and pyromellitic acid showed fairly good chelation effects. Zeolite was the least effective and zeolite-support of citric acid (Na-cit.zeo) was the most effective chelant among all the chelating agents tested. Na-cit.zeo showed a synergistic effect over the combined chelation efficiency of zeolite and citric acid at the same concentration level. The results are presented in Figure 1.

Figure 1. Effect of concentration of chelants with and without zeolite support on Mn content of TMP. Temperature 60°C, time 30 min., pH 5.5.



This experimental evidence suggests that the impregnation of a chelant such as citric acid, on a porous zeolite support could be an efficient way to achieve heavy

metal chelation in pulp. Two possible explanations can be provided for this improved metal chelation effect. Firstly, zeolite might decrease the water hardness by effective chelation of non-transition metals, which could increase the amount of free organic acid available for transition metal chelation. It can also be argued that once an organic acid scavenges a heavy metal ion, the organic acid-metal ion chelate complex can now involve in a further ion exchange reaction with porous zeolite. Such ions exchange process would then regenerate the free organic acid. The liberated organic acid is capable to undergo further exchange reaction with metal ion present in pulp. However, there is no experimental proof for these arguments. **Figure 2** shows the effects of pretreatment of TMP with an optimum concentration of each zeolite- support chelant (2 wt% of adsorbed acid on 1% zeolite support). It also compares the above results with a 0.5 wt% DTPA pretreated pulp. The water insoluble zeolite is least effective for Mn. The chelation efficiency was increased in the following order: Na-cit.zeo > Na-pyromel.zeo > zeolite. The chelation performance of Na-cit.Zeo was comparable to DTPA. Figure 1 presents the initial metal contents of the pulp used in these experiments.

Figure 2. Effect of type of chelants on metal content of TMP; temperature 60°C, time 30 min. and pH 5.5.

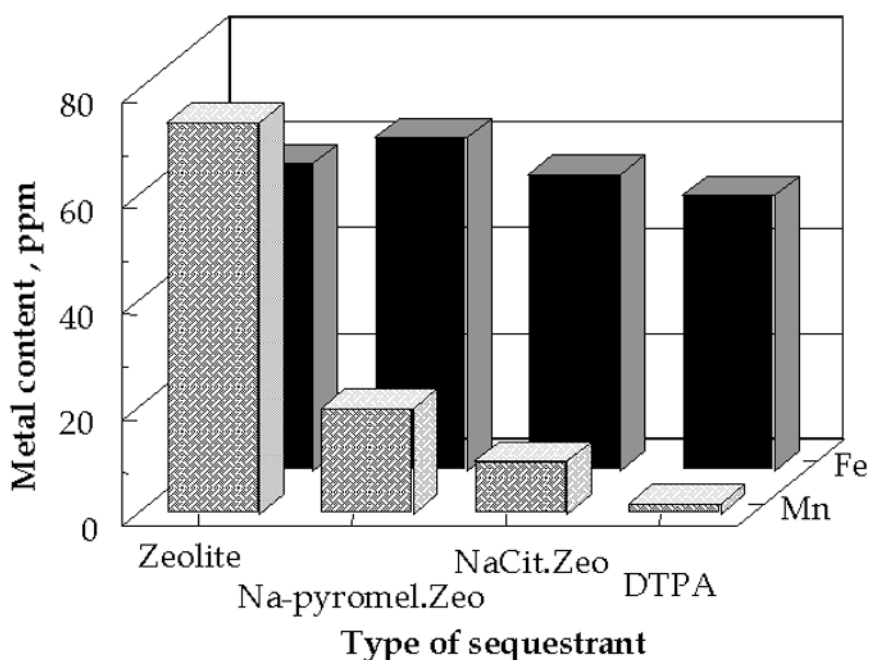


Table 2. Experimental design parameters for pretreatment with Na-cit.zeo system

Factors	-1	+1
Temperature, °C	50	70
Time, min	30	60
pH	5.5	8.5

Based on our preliminary results we designed a three-factorial statistical experimental plan to optimize the pretreatment conditions for Na-cit.zeo system. **Table 2** gives the experimental parameters for determining the effect of temperature, time and pH of pretreatment with 2% Na-citrate being supported on 1% Na-A zeolite. For each set of experiment Cu, Fe and Mn contents were determined after pretreatment. Statistical analysis of the experimental results revealed that the F-test values were very low for all the parameters studied for Cu and Fe. It was due to the fact that the initial concentration of Cu was very low and the Fe concentration in the pulp did not decrease enough even after chelation to render this parameter statistically significant. Therefore, it was concluded that the pretreatment parameters in the given experimental range did not influence the Cu and Fe contents in the pulp. Nonetheless, some of the chelation parameters showed statistically significant effects on Mn concentration. For Mn chelation, the F-test values for pH, temperature and time were 23.6, 3.5 and 0.8 respectively. Hence Mn concentration in pulp was very much influenced by the pH of the pretreatment solution in the presence of Na-cit. zeo. Temperature is also of significance for Na-cit.zeo chelation system. A regression equation involving the statistically significant experimental parameters and the

Mn concentration in pulp is given by equation (1). The correlation coefficient (R^2) for this equation is 0.8.

$$\text{Mn (ppm)} = 20.9 + 13.1 * (\text{pH}) - 2.88 * (T) - 2.02 * (\text{pH} * T) \quad \text{Eq. (1)}$$

where T is the pretreatment temperature.

The regression equation (1) shows that neither the pH nor the temperature is a linear function of Mn concentration. A high alkalinity has a negative effect on pretreatment efficiency. It is interesting to note that the interactive effect of pH and temperature is positive toward Mn chelation. Therefore, a higher pretreatment temperature can offset the negative influence of high alkalinity on Mn chelation. Statistical experimentation further revealed that the pretreatment time had no practical significance on metal chelation. The reason for this observed statistical effect was not clear. It was thought that the observation was a consequence of choosing an ineffective time range (30 to 60 min) for pretreatment in the given experimental design, i.e. the lower limit of the pretreatment time was too long to note any effect of time change. In order to verify the validity of this argument we carried out some classical experiments by varying pretreatment time from 5 to 30 min **Figure 3** illustrates this effect. Obviously at a high temperature such as 70 °C even 5 min pretreatment time was sufficient to achieve an effective chelation of Mn. However, a somewhat different result was obtained at a lower temperature. At 60 °C, an increase in the pretreatment time from 5 to 30 min decreased the Mn content in pulp continuously. The results from the statistical experimental design demonstrated that the best chelant was a composition of 2% Na-citrate supported on 1% Na-A zeolite. The optimum pretreatment condition was 60°C and 30 min. **Table 3** summarizes the results of the Na-cit.zeo system under the optimum condition as described above. Table 3 also shows the results of a DTPA pretreatment as a control [2]. From above results it can be concluded that Na-cit.zeo system is a

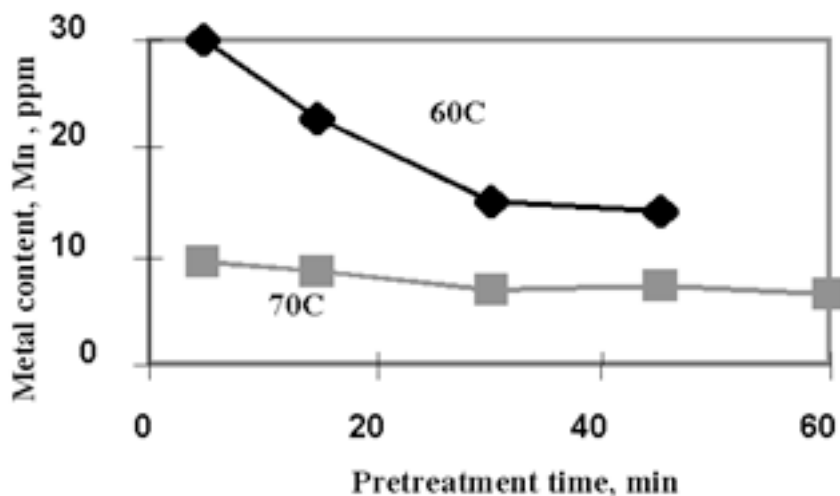
technically viable alternative to DTPA as a pretreatment chemical. The optimum concentration of Na-cit.zeo was somewhat high (2 wt%) in the example presented in this report. It is important to mention that the cost factor was not included in optimizing the process condition.

Table 3. Metal content profile for DTPA and Na-cit.zeo systems

Pretreatment*	Mn , ppm	Cu, ppm	Fe, ppm
No pretreatment	101± 5.6	2.5± 0.64	110± 7.3
DTPA (control)	2.1± 0.9	1.4± 0.1	52± 3.5
Na-cit.zeo (alternative)	13 ± 1.7	1.0± 0.05	56± 2.9

* 0.4 % by weight of 40 % active DTPA at 60°C for 30 min, pH5.5;
2% Na-citrate supported on 1% Na-A zeolite at 60°C for 30 min, pH 5.5.

Figure 3. Effect of pretreatment time of zeolite support of Na-citrate on Mn content of TMP. Na-cit.zeo. :2.0 % by weight of pulp, pH: 5.5.



Bleaching

Na-silicate is an effective stabilizer for hydrogen peroxide bleaching of TMP. Earlier it was reported that Na-silicate could be replaced by DTPMPA in

order to minimize or avoid scaling [6]. We found that zeolite support of a polyamino phosphonic acid designated here, as Phos.Zeo is an effective peroxide stabilizer for TMP brightening. The efficacy of Phos.Zeo is attributed to its contribution toward achieving good brightness gain of pulp at a significantly low peroxide consumption. It also helped to reduce alkali charge in the bleach liquor. Moreover, the addition of Phos.Zeo in peroxide bleach liquor generates less COD, TOC and dissolved organic in the bleach effluent. The peroxide stability in the bleach liquor was found to depend on the concentration of the Phos.Zeo, the ratio of NaOH/H₂O₂, and also on the weight percent of the polyamino phosphonic acid impregnated on zeolite. **Figure 4** and **Table 4** summarized these findings. As pulp brightness and peroxide consumption were sensitive to peroxide bleach stability, the efficacy of Phos.Zeo was estimated from brightness gain and residual peroxide concentrations in a bleaching trial.

Figure 4. Effect of Phos.Zeo concentration on ISO brightness gain; initial brightness of Na-cit.zeo pretreated pulp 57.5% ISO, 12% consistency, 70°C, 2h, 2.5 wt% H₂O₂, 0.05% MgSO₄, NaOH/H₂O₂ 0.8. The amount of adsorbed phosphonic acid is 3, 20 and 50 percent by weight of Phos.Zeo respectively for curves 1, 2 and 3.

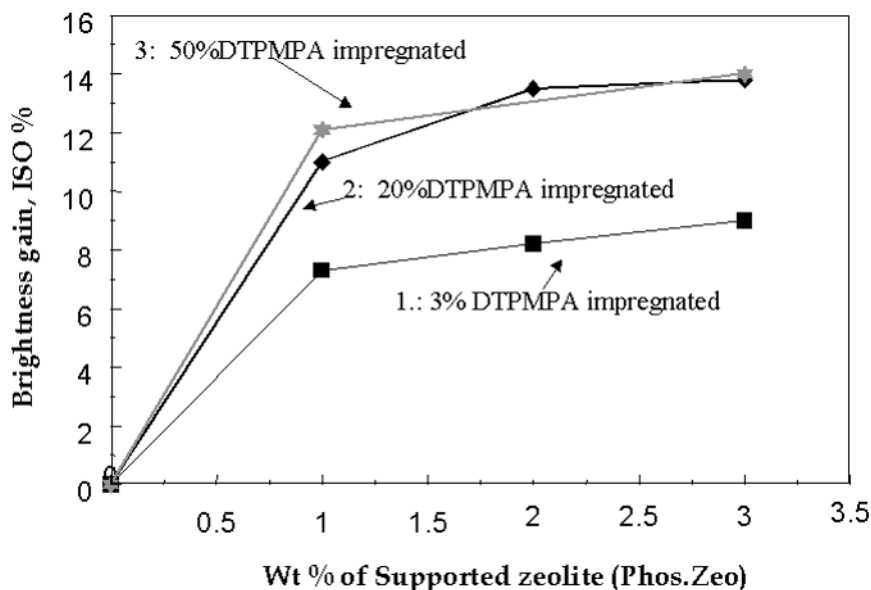


Table 4. Effect of NaOH/H₂O₂ ratio on TMP bleaching*

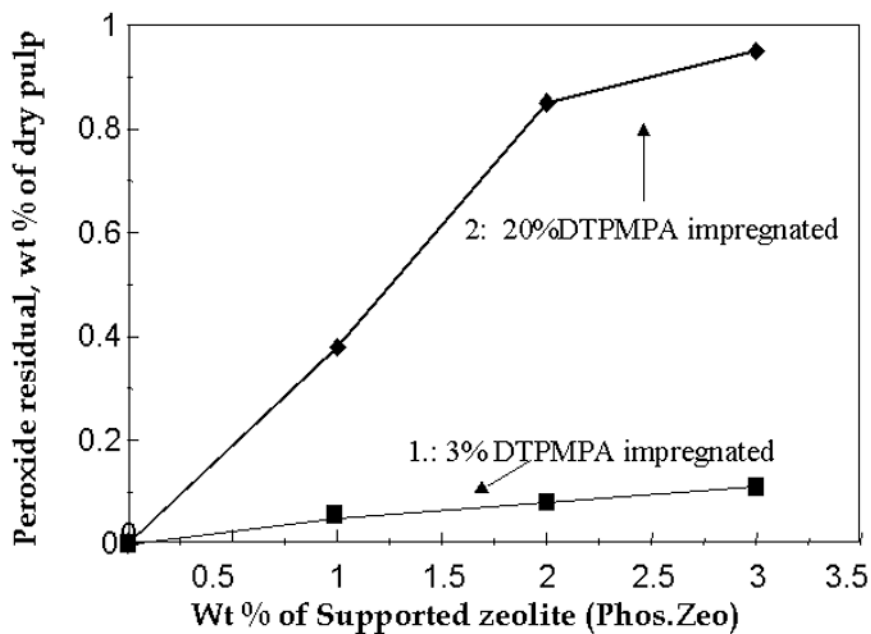
NaOH/H ₂ O ₂	0	0.4	0.8	1.2
pH after bleaching	6.3	7.7	7.9	8.7
% ISO gain	4.3	11.8	13.8	13.5
%res. peroxide	1.6	1.31	0.94	0.46
%residual NaOH	0	0	0.15	0.59
Change in b*	-	-0.68	-0.47	-0.22

*Pretreatment and bleaching conditions are the same as in Figure 4 with 3 wt% Phos.Zeo (20% adsorbed phosphonic acid derivative).

Figure 4 shows the effects of concentration of Phos.Zeo and concentration of the phosphonic acid in Phos.Zeo on pulp brightness gain. Bleaching conditions are given in figure caption. Increasing Phos.Zeo concentration increased brightness until a plateau was achieved at about 3 wt%.

The effect of the concentration of adsorbed polyamino phosphonic acid on pulp brightening was more prominent. Increasing polyamino phosphonic acid concentration from 3 to 20% by the weight of total support has a significant positive effect on the pulp brightness. A similar effect was also observed for the residual peroxide content after bleaching. The effects of the Phos.Zeo charge and the effect of the concentration of the adsorbed polyamino phosphonic acid on residual peroxide content can be seen in **Figure 5**. A zeolite support stabilizer containing 20% of the adsorbed phosphonic acid significantly increased the residual peroxide content compared to a supported stabilizer containing 3% of the adsorbed acid. A further increase in the impregnated polyamino phosphonic acid content from 20 to 50 percent had no practical advantage. Therefore, an effective concentration of phosphonic acid was found to be 20% on zeolite support.

Figure 5. Effect of Phos.Zeo concentration on residual peroxide; pretreatment and bleaching conditions are the same as in Figure 4. Weight% of adsorbed phosphonic acid is 3% and 20% respectively for curves 1 and 2 and is the same as in Figure 4.



The effect of the alkalinity on the peroxide stabilization was studied by varying the NaOH/H₂O₂ ratio. It was found that the pulp brightness could be influenced by alkali/peroxide ratio. The brightness gain was highest for a NaOH/ H₂O₂ ratio of 0.8, which is evident from the results shown in Table 4.

From these preliminary results it became obvious that an optimization of three bleaching parameters, concentrations of peroxide, NaOH and Phos.Zeo, were required in order to determine the overall efficiency of zeolite support chemicals. Table 1 gives the optimization parameters. The results of the regression analyses and the ANOVA (analysis of variance) of the planned experimental design involving three independent variables and three response variables are given in **Table 5**.

Table 5. Regression coefficients and statistical parameters of bleaching optimization model

Effects	ISO%	b*	Res.Per. %
Regression constant	68.1	12.3	1.61
Linear effects			
H ₂ O ₂ , wt%	1.94	-0.42	0.71
Phos.Zeo., wt%	0.48	-0.2	NS
NaOH, wt%	1.32	NS	-0.27
Interaction effects			
H ₂ O ₂ *Phos.Zeo	0.96	0.37	NS
H ₂ O ₂ *NaOH	NS	-0.61	NS
NaOH*Phos.Zeo.	NS	NS	NS
R ²	0.90	0.75	0.86
F-ratio	23	31	36

*NS- statistically not significant; level of confidence 0.95

The optimization of the independent variables revealed that the most effective stabilization could be achieved by adding 3 wt% of the Phos.Zeo stabilizer in the bleach liquor at 70 °C and then bleaching the pulp for 2h. The stabilizer was composed of 20% of the polyamino phosphonic acid adsorbed on 80% of Na-A zeolite. The optimized amount of hydrogen peroxide charge was 2.5 wt% and NaOH/H₂O₂ weight ratio was 0.6.

Phos.Zeo stabilizer and other systems

Table 6. Effect of optimized alternative pretreatment and stabilization systems on pulp properties

Nature of pretreatment	DTPA at 60°C for 30 min, pH5.5		Na-cit.zeo at 60°C for 30 min pH 5.5		
Bleaching					
[Phos.Zeo], wt%	-	3.0*		3.0*	
Na-silicate, wt%	3.0	-			3.0
DTPMPA, wt%	-	-	0.6	-	
[H ₂ O ₂], wt%	2.5	2.5	2.5	2.5	2.5
[NaOH]/ [H ₂ O ₂]	0.8	0.6	0.8	0.6	0.8
ISO % gain	9.8	11.8	12.7	13.6	10.8
b* change	-1.3	-0.43	-0.64	-0.74	0.28
Res. peroxide, %	0.97	1.1	0.85	1.4	0.72

- Contains 0.6 wt% (o.d. pulp basis) DTPMPA impregnated in zeolite; COD for DTPA/Na-silicate = 33.8 kg/Ton; COD for Na-cit.zeo/Phos.Zeo. = 14.6 kg/Ton;

The bleach stabilization performance of Phos.Zeo was compared with alkaline Na-silicate. **Table 6** compares the bleaching results of a zeolite support chelant (Na-cit.zeo) and Phos.Zeo stabilizer with a commercially used chelant/stabilizer system such as DTPA/Na-silicate at their optimum concentration [7]. We also compared the bleach stabilization efficiency of Phos.Zeo system with the unsupported polyamino phosphonic acid [7]. The best system was found to be a Na-cit.zeo pretreatment of pulp followed by bleach stabilization with Phos.Zeo. The additions of 0.6% DTPMPA showed better stabilization effect over 3% Na-silicate [6]. Overall performance was best for the Phos.Zeo system. The addition of 2.5% of Phos.Zeo gave a higher brightness gain over the control system at a lower peroxide consumption. Again,

Phos.Zeo stabilizer was effective both for the DTPA and the Na-cit.zeo pretreated pulps. However, the Na-cit.zeo pretreatment showed marginally better results with respect to brightness gain and residual peroxide content over the DTPA pretreatment. The chemical oxygen demand (COD) of the bleach effluent obtained by employing zeolite support systems was less than the conventional DTPA/Na-silicate system. A possible explanation is a reduced alkali charge in bleach liquor with the zeolite support system as documented in Table 6. Another explanation of this reduction of the COD value can be the effect of adsorption of colloidal and dissolved organic matters on porous zeolite on during the bleaching reaction.

System closure

Table 7. Effect of white water recycling on bleaching*

Properties	Brightness Gain		b* Coordinate		Opacity, ISO%	
Water quality	Phos.Zeo	Silicate	Phos.Zeo	Silicate	Phos.Zeo	Silicate
Deionized water	10.8	11.1	11.6	11.2	90	88.6
Recycled white water	11.2	9.9	11.3	11.9	91.4	86.7
Treated water	10.9	10.7	11.3	11.5	-	-
Bleach effluent characteristics	TOC, mg/L		COD, kg/T		Turbidity, FAU	
Na-silicate	480		29.7		689	
Phos.Zeo	298		18.9		640	

*2 wt% peroxide, 1.8 wt% NaOH and 3 wt% stabilizer*2 wt% peroxide, 1.8 wt% NaOH and 3 wt% stabilizer;

Table 7 demonstrates the results of the effect of recycling bleaching effluent on the bleaching process. The examination was carried out using two separate bleach compositions. Although the concentrations of peroxide, alkali and stabilizers were kept constant, the chemical compositions of stabilizers were different. Two different studies were made. In one case, white water after bleaching was recycled without any treatment and in another case white water was treated in a lab-scale DAF unit with 50 ppm of a cationic polyacrylamide

flocculent. Evidently, recycling of untreated white water obtained from the Phos.Zeo containing bleach liquor showed favorable brightness and opacity results. There was no brightness loss over fresh water supply and the opacity of the bleached pulp was increased marginally. Predictably, this increase in opacity was due to the deposition of zeolite on the fiber surface. In contrast, recycling of Na-silicate containing bleach liquor negatively influenced the pulp brightness. The results from the recycling of treated water showed no measured difference in pulp brightening. The marginal detrimental effect of Na-silicate containing white water system on pulp brightness can be attributed to higher colloidal and dissolved organic matter contents as evident from the TOC and COD values.

Conclusions

Zeolite supports of pretreatment agent and stabilizer are efficient bleaching chemicals. These supported chemicals demonstrated better chelation and peroxide stabilization efficiency compared to an optimum charge of conventional DTPA/Na-silicate system. A pretreatment with 2 wt% Na-cit.zeo of a commercial TMP chelated Mn and Fe effectively under a mildly acidic pH condition. Concentration of Na-cit.zeo was influenced by the amount of adsorbed citric acid on zeolite support. Time of pretreatment can be decreased to 10 min or less by increasing the pretreatment temperature to 70 °C. An optimum pretreatment condition of 30 min at 60 °C was recommended.

Phos.Zeo was a more effective peroxide bleach stabilizer compared to Na-silicate or DTPMPA. The stabilization efficiency was dependent on the amount of adsorbed polyamino phosphonic acid, the ratio of NaOH/H₂O₂ and the weight % of Phos.Zeo added. Best effect of stabilization was obtained for a 3 wt% Phos.Zeo containing 20% adsorbed diethylene triamine penta-methylene phosphonic acid by weight of zeolite at 0.6 NaOH/H₂O₂ ratio. Phos.Zeo can totally replace Na-silicate in bleach liquor stabilization with an overall gain in pulp brightness and residual peroxide. Recycling of bleach effluent containing

zeolite support chemicals had no detrimental effect on pulp brightening and opacity of pulp improved by circulating bleach effluent.

REFERENCES

1. Eul, W.; Suss, H.U.; Moglichkeiten und Grenzen des Deinkingprozesses, Wochenbl. fur Papierfab. **116** (6) 224-231 (1988).
2. Dorica, J., Ramamurthy, P., Eillot, A., Crotogino, R, Vrooman, W., Chatterjee, A., and Wong, P., "Mill Studies on closure of the effluent cycle in a newsprint mill". Paprican Pulp and paper Report 1152, (1995);
3. Sullivan, D., and Kasper, J.K., "Whitewater recycle feasibility study for James River-Otis, Jay, Maine" TAPPI Environmental Conference Proceedings, 1990, page 151.
4. Prasakis, J., Sain, M. and Daneault, C.; "Metal management improves peroxide bleaching of TMP"; Tappi J. Vol.79, no. 10 , 48-53, 1996.
5. Putz, H.-J., Ackermann, C., Gottsching, L., "Bleaching of wood containing DIP with alternative chemicals – possibilities and limitations"; Int. Conf. Proceedings , PIRA 4th Int. Wastepaper Conf., p. 189-219; June 13-15, 1995.
6. Supported Catalyst; A.R. Bull and J.T. McManamon; ACS symposium Service (1990), 422, 1989; Bleach activators; W.E. Paget, UK patent no. GB 2 249 104 A, April, 1992.
7. Sain, M. M. and Daneault Claude; "Prebleaching and Postbleaching of ONP with alternative chemicals: Chances and limitations", Pulp and Paper Canada; 98 (9) 49-53 (1997).
8. Leonhardt, W.; Schmidt, K.; Suss, U.H. and . Glaum, H; "Use of zeolite in bleaching"; German Patent DE 4118899, October, 1992.
9. Arbil, P.A., Suarez, R. and Rodriguez, M.; "Use of synthetic zeolite as charge in high grammage paper"; Inv. Tec. Papel; no. 115, 9-16, 1993.

10. Kuczynski , K., . Niji , H., and May, B. H.; “DTPMPA: polyamino polyphosphonic acid and its use in paper processes”; Tappi J., Vol. 70, (6) 171-174, 1988.