CELLULOSE CHEMISTRY AND TECHNOLOGY

IMPROVING THE BLEACHING PROCESS OF HARDWOOD CHEMI-MECHANICAL PULP

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Received December 31, 2013

In the first phase, the effect of different NaOH to H_2O_2 ratios on bleaching chemi-mechanical pulp (CMP) was investigated. The pH of unbleached pulp was 5.25 and its brightness and freeness were 37.5 and 745 ml respectively. Results indicated that the brightness increased by growing the peroxide charge, but the increase in the NaOH percentage had inhomogeneous effects. As data showed, the best brightness values were found with 0.75 NaOH/H_2O_2 ratios. High ratios led to a noticeable upward trend in pulp yellowness, while ratios below 0.75 resulted in lower brightness. In the second phase, the effects of replacing NaOH by $Mg(OH)_2$ were examined. Results showed that this replacement determined an improvement in the optical properties and pulp yield. However, the mechanical properties were similar in both processes. Also, this replacement led to a decrease in the Chemical Oxygen Demand (COD) and conductivity in the bleaching effluent. The residual peroxide in the $Mg(OH)_2$ bleaching process was higher than in the NaOH bleaching process.

Keywords: bleaching, hydrogen peroxide, sodium hydroxide, magnesium hydroxide, Chemical Oxygen Demand, bleaching effluent

INTRODUCTION

Alkaline peroxide bleaching is one of the most common processes for high yield pulp bleaching. In this process, the bleaching agent is a hydroperoxide anion, which is produced by the decomposition of hydrogen peroxide under alkaline conditions, according to Equation 1:

$$H_2O_2 + OH^- \rightarrow H_2O + HOO^- \qquad (1)$$

As Equation 1 indicates, an alkaline environment is needed to form an active hydroperoxide anion.[1] Also, alkaline conditions lead to fiber swelling, which causes both improving of bleach liquor penetration and accessibility of the chromophore groups. However, high concentration of the hydroperoxide anions causes decomposition of hydrogen peroxide, especially at elevated temperatures (Eq. 2). Therefore, it is common practice to add sodium silicate as a stabilizing and buffering agent, and also, the pH value must be controlled by changing the alkali ratio in the bleach liquor.[2]

$$HOO^- + HOOH \rightarrow HO_2\bullet + HO\bullet + OH^- \qquad (2)$$

Thus, very high pH should be avoided. The optimum amount of caustic soda depends not only on the amount of peroxide to be reacted, but also on the temperature level and the retention time.[3] Moreover, high contents of alkali substances, and, then, high pH values bring about a phenomenon, which has been called alkaline darkening in the pulp bleaching process (Eq. 3).[3,4] Hence, it is necessary to find a suitable ratio of alkali to peroxide in the bleaching process.

$$\text{Lignin} + OH^- \rightarrow \text{chromophore groups} \qquad (3)$$

This ratio, which depends on the type of pulp, chemical treatment in the pulping process, bleaching process conditions etc., is about 0.6 to 0.8. In acid based pulps (acid pretreatments), the pH of the pulps is acidic (pH<7), and the consumption of alkali is higher than with other pulps.[5,6] Actually, the initial and final pH in the pulp bleaching process must be kept at an ideal value, which for the pH in bleaching at 65 °C to 70 °C is typically between 8.5 and 9.0.[3]

The first phase of this research aimed to investigate the effect of different chemical consumption values on the optical and physical properties of CMP, and also to find the best alkali to peroxide ratio in the bleaching process of CMP.

In the second phase, the effect of replacing caustic soda by magnesium hydroxide (in the bleaching process) on the bleached pulp properties was investigated. The alkali to peroxide ratio, which was constant according to calculations done in the first phase, was a noticeable point in this phase. The peroxide bleaching with $Mg(OH)_2$ of high yield pulps has been recently developed in the pulp and paper industries.[7] The associated benefit includes decreased bleaching cost, decreased chemical oxygen demand COD, less anionic trash, and improved optical and physical strength properties of the bleached pulps.[8-10]

The nucleophile destruction of conjugated side chains and of quinones is complemented favorably by the inability of the hydroperoxide anion (HOO^-) to destroy aromatic rings. This maintains a high proportion of lignin in the pulp and keeps the opacity high. For bleaching mechanical pulp, no other similarly simple and inexpensive nucleophile chemical is available. Electrophiles would react with the aromatic structures and either remove lignin or generate the potential for more chromophores. Today, the main problem in peroxide bleaching is the amount of organic material dissolved under the alkaline bleaching conditions. Alkalization with magnesium hydroxide or calcium hydroxide can be an alternative, as they dissolve less lignanes and polyoses.[3] The milder alkalinity of the $Mg(OH)_2$ system is believed to be the cause of more effects of this alkali source on pulp and bleaching process properties, such as the lower COD formation. The higher COD values of NaOH were attributed to its strong alkalinity; with creating a high-pH environment, the longer chain molecules in the pulp hydrolyze to smaller and soluble ones.[11] Another advantage of the $Mg(OH)_2$ alkali is its low solubility, which results in a lower pH.[12] The low solubility of $Mg(OH)_2$ allows it to provide a constant alkalinity at various alkali charges, and also pH values are approximately constant during the bleaching, while initial and final pH values mark a significant difference in NaOH-based process.[2]

EXPERIMENTAL

Materials

Unrefined CMP from a mixture of some hardwoods (sulfite process) was obtained from Mazandaran Wood and Paper Company. The wood species used were hornbeam, beech, and birch in a mixture percentage of 60, 20, and 20, respectively. The brightness of unbleached pulp was 37.5% ISO, and its freeness was 745 ml (CSF). All chemicals used were of analytical grade and all chemical charges were calculated based on oven-dried pulp weight.

Chelation stage

Chelation of pulp was performed at 3% pulp consistency, pH 4.5-5.5, and 70 °C for 30 minutes, with 0.3% DTPA (Diethylene Triamine Pentaacetic Acid). Then, the pulp suspension was thickened to about 25% consistency by 325-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines.

Bleaching stage

Bleaching experiments were conducted in polyethylene bags using the following conditions: 2-4% H_2O_2, 1.5-3.0% NaOH or 1.2-2.4% $Mg(OH)_2$, 3% sodium silicate (water glass), 0.2% Epsom salt ($MgSO_4.7H_2O$), 0.1% DTPA, 10% pulp consistency, 70 °C, and 120 minutes. The alkali source in the first phase was just NaOH. Also, in this phase, the alkali to peroxide ratio was not constant, as shown in Table 1.

In the second phase, the alkali to peroxide ratio was constant, which means 0.75 for the NaOH-based process, and 0.6 for the $Mg(OH)_2$-based process (Table 2). The used values of $Mg(OH)_2$ for hydroxyl ion production, which was determined by acid titration, were equal to NaOH in those treatments with the same peroxide charges. The rate of magnesium hydroxide to sodium hydroxide consumption was 0.8. The chemicals were mixed in a beaker in the following order: water, sodium silicate, sodium hydroxide or magnesium hydroxide, Epsom salt, DTPA, and then hydrogen peroxide. The prepared bleach liquor was then added to the pulp, which had been heated to the reaction temperature, and good mixing was provided by kneading. The polyethylene bag was sealed and placed into a water bath for the desired retention time at the set temperature. After the completion of the bleaching time, the pulp sample was cooled down with cold running water to room temperature and diluted to 1% suspension with deionized water. The well-mixed pulp suspension was then filtered by a 325-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines. The resultant filtrate was further filtered with a Whatman mediumfast filter paper to remove residual fines, and then used for determining the conductivity and COD load of the bleaching effluent.

Pulp mechanical testing

Bleached pulps were refined to a target freeness (350 ml CSF), using a Labtech PFI machine according to the TAPPI standard methods. Handsheets were prepared and optical, physical and mechanical properties were measured. All steps of handsheet making and measurement of paper properties were done according to the TAPPI standard methods.[13]

Table 1
First phase bleaching conditions

Treatment code	H_2O_2, %	NaOH, %	Alkali ratio ($NaOH/H_2O_2$)
A1	2	1.20	0.60
A2	2	1.50	0.75
A3	2	1.80	0.90
B1	3	1.80	0.60
B2	3	2.25	0.75
B3	3	2.70	0.90
C1	4	2.40	0.60
C2	4	3.00	0.75
C3	4	3.60	0.90

Table 2
Second phase bleaching conditions

Process type	NaOH-based process			$Mg(OH)_2$-based process		
Treatment code	A	B	C	D	E	F
H_2O_2, %	2	3	4	2	3	4
NaOH, %	1.50	2.25	3.00	-	-	-
$Mg(OH)_2$, %	-	-	-	1.20	1.80	2.40
Alkali ratio[a]	0.75	0.75	0.75	0.60	0.60	0.60

[a] NaOH or $Mg(OH)_2/H_2O_2$

RESULTS AND DISCUSSION

First phase

In this phase, the ratio of alkali ($NaOH/H_2O_2$) was investigated to modify the bleaching process to gain the best properties of the bleached pulp. As shown in Table 3, the optical properties of the bleached pulps were raised by a peroxide charge increase. Also, at equal peroxide charges, the treatments at 0.75 alkali ratio showed the best optical properties.

In the peroxide bleaching process, the alkali is needed to activate hydrogen peroxide by forming reactive hydroperoxide anion species. However, a too high concentration of hydroperoxide anions, with a high pH value, causes the decomposition of hydrogen peroxide, especially at elevated temperatures. Therefore, it is common practice to add sodium silicate as a stabilizing and buffering agent.[2] Furthermore, a high level of alkaline substances and accordingly, high pH values determine the creation of new chromophore groups in the pulp (Eq. 3).[3,4] Hence, the yellowness of the bleached pulp was increased by intensifying the alkali rate at the same peroxide charge (Table 3).

As shown in Table 3, the opacity of the handsheets was decreased by raising the peroxide charge for all alkali amounts, but the opacity values had the least quantity at the alkali ratio of 0.75. Also, the opacity had an inverse relationship with the brightness value and it increased along with an increase in yellowness.

The opacity property of paper sheets is influenced by thickness, porosity, value and type of filler, bleaching degree of fibers, coating, and the like.[13] Porosity increases light scattering in paper layers, thus, it reinforces the opacity. The bonding area was enhanced, and so porosity decreased, as the bleaching degree increased.

Figure 1 shows the yield of bleached pulp under various bleaching conditions. At constant peroxide levels, the yield of bleaching was decreased by the increase in alkali charge.

The selectivity of the bleaching process is one of the best factors to evaluate and to measure the process efficiency. This factor is the rate of brightness increase to yield loss, which is determined by Eq. 4:

$$B.s. = (F.b. - I.b.)/Y.l. \tag{4}$$

where B.s.: Bleaching selectivity; F.b.: Final brightness; I.b.: Initial brightness; Y.l.: Yield loss (100-pulp yield).

The selectivity factor had the highest amount at 0.75 alkali ratio (Fig. 2). Thus, the ratio of 0.75 was chosen as the optimum alkali ratio for the second phase of hardwood CMP bleaching.

Table 3
Pulp optical properties in the first phase

Treatment code	Alkali ratio	Brightness, %	Opacity, %	Yellowness index
A1	0.60	70.2	88.4	6.17
A2	0.75	72.6	88.2	6.10
A3	0.90	70.9	88.3	6.19
B1	0.60	72.6	87.6	5.88
B2	0.75	74.0	87.6	5.82
B3	0.90	73.5	87.7	5.91
C1	0.60	74.6	87.0	5.63
C2	0.75	76.0	86.7	5.24
C3	0.90	75.4	86.8	5.35

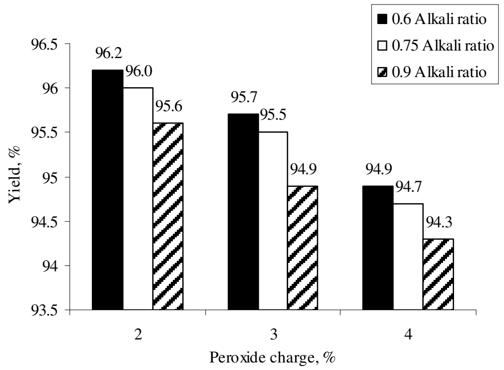

Figure 1: Yield of bleached pulps in the first phase

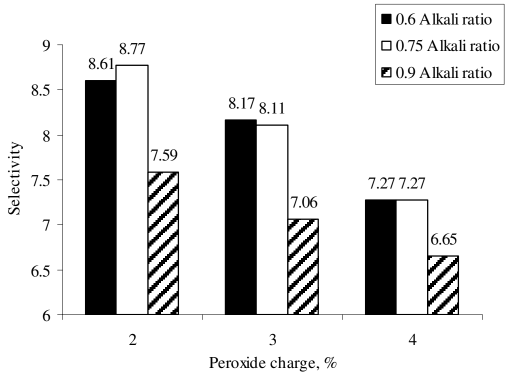

Figure 2: Bleaching selectivity in the first phase

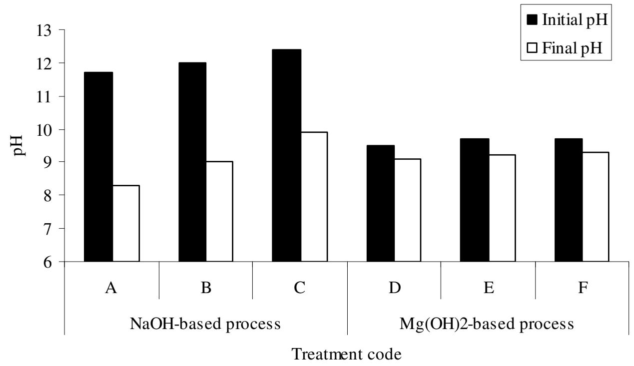

Figure 3: Initial and final pH in the $Mg(OH)_2$ and NaOH processes

Table 4
Pulp optical properties at second phase

Process type	NaOH-process			$Mg(OH)_2$-process		
Treatment code	A	B	C	D	E	F
Brightness, %	72.6	74.2	76.0	73.2	75.9	77.8
Opacity, %	88.2	87.5	86.7	88.1	87.3	86.5
Yellowness index	6.10	5.82	5.24	5.75	4.73	4.11

Second phase

Magnesium hydroxide is an alkali substance consisting of one magnesium cation and two hydroxide anions bound by an ionic bond. This alkali has low solubility in water and so its alkalinity is less than that of sodium hydroxide.[14] In the conventional bleaching process (NaOH alkali source), alkalinity or hydroxide anion concentration was high at the beginning of bleaching, as a result of the high solubility of caustic soda in water (Fig. 3). The pH values in this process were not constant during the reaction time, so the highest and lowest values were observed at the initial and final time, respectively. The inhomogeneous pH has been reported to have negative effects on pulp bleaching.[2] A high concentration of the hydroxide anion leads to an increase in the hydroperoxide anion, and a too high concentration of the hydroperoxide anions causes the decomposition of hydrogen peroxide, especially at elevated temperatures. Therefore, it is a common practice to add sodium silicate as a stabilizing and buffering agent. By using $Mg(OH)_2$ in the bleaching process, a homogeneous pH will be established during pulp bleaching, because this alkali has low solubility in water (Fig. 3).

As shown in Table 4, the brightness values of the $Mg(OH)_2$-based process were higher than those of the NaOH-based process at the same H_2O_2 charge, but no significant difference in opacity was observed between the two bleaching processes. The yellowness values of the bleached pulps by the $Mg(OH)_2$-based process were lower than those of the NaOH-based process at the same H_2O_2 charge.

These results can be explained by the milder alkalinity of $Mg(OH)_2$, because of that, alkaline darkening decreased. The phenomenon of alkaline darkening appears because of a high concentration of the hydroxide anion in the pulp suspension environment.[3,4] The low solubility of $Mg(OH)_2$ contributed to a constant alkalinity at various alkali charges, and also as shown in Figure 3, pH values were approximately constant during the bleaching process. Vice versa, the sodium hydroxide is an excellently soluble alkali, which leads to a heavy load of hydroxide anion in the primary reaction. Thus, there was a significant difference between initial and final pH in the NaOH-based process, under these conditions new chromophore groups were created in the pulp (Eq. 3).[3]

It may be noted from Table 5 that both processes led to similar mechanical properties. Also, the mechanical properties improved by increasing the chemical charges. Factually, more reactions and a more intense process under high chemical charges resulted in a higher fiber collapsibility and more bonding areas. Therefore, the mechanical properties improved, and paper bulk decreased.

According to Table 6, the $Mg(OH)_2$-based and the NaOH-based bleaching processes produced bleached refined pulps with similar tensile and burst strength. The tear strengths of the $Mg(OH)_2$-bleached pulps were higher than those of the NaOH-bleached pulps. Little bleaching damage of the $Mg(OH)_2$-based process, as well as the higher beating of the $Mg(OH)_2$-bleached pulp led to an increase in tear strength.[15]

Figures 4 and 5 indicate that the initial freeness of the bleached pulps, and the refining values to reach the target freeness (350 ml) decreased by increasing the chemical charges for both bleaching processes. Fiber swelling, improvement of fiber collapsibility, removal of hydrophobic compounds and creation of hydrophilic functional groups upon a decrease in the DP of macromolecules, as well as the unbraiding structure of the fiber at high chemical charges, are all possible reasons for this.[12,16]

Conventionally bleached pulps had lower initial freeness than those of the $Mg(OH)_2$-based process (Fig. 4). Moreover, the refining values of conventionally bleached pulps to reach the target freeness were lower than those of the $Mg(OH)_2$ bleached pulps (Fig. 5). These results can be explained by the stronger reaction conditions of the NaOH-based process and accordingly, the higher production of hydrophilic functional groups and fiber swelling in this process.[16-17]

Figure 6 shows the yield of bleached pulp under various bleaching conditions. Evidently, the bleaching yield from the $Mg(OH)_2$ process was higher than that of the NaOH process. The difference increased significantly as the chemical charges rose because the bleaching conditions were more severe for the NaOH process. For example, at 4% peroxide charge, the bleaching yield was 97.18% for the $Mg(OH)_2$ process, compared to 95.54% for the NaOH process. The yield gained from the $Mg(OH)_2$ process would represent a significant economic benefit for the pulp and paper factories that would adopt this process.

Table 5
Mechanical properties of unrefined pulps

Process type	NaOH-process			$Mg(OH)_2$-process		
Treatment code	A	B	C	D	E	F
Tensile index (Nm/g)	31.1	36.5	39.5	30.9	35.8	39.2
Burst index (KN/g)	2.21	2.24	2.26	2.19	2.22	2.26
Tear index (mNm^2/g)	6.67	6.70	6.72	6.66	6.72	6.74
Bulk (cm^3/g)	2.42	2.39	2.35	2.43	2.40	2.36

Table 6
Mechanical properties of refined pulps

Process type	NaOH-process			$Mg(OH)_2$-process		
Treatment code	A	B	C	D	E	F
Tensile index (Nm/g)	63.2	64.5	67.1	63.9	64.6	66.8
Burst index (KN/g)	4.69	4.81	5.02	4.72	4.84	4.98
Tear index (mNm^2/g)	7.65	7.80	7.78	7.91	7.98	8.02
Bulk (cm^3/g)	2.19	2.11	2.05	2.21	2.11	2.06

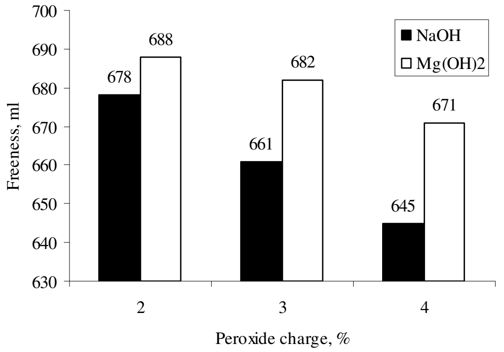

Figure 4: Initial freeness of $Mg(OH)_2$ and NaOH bleached pulps

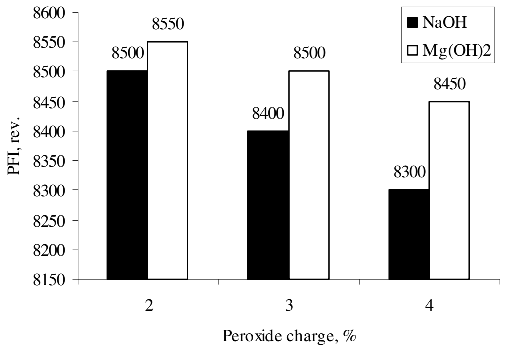

Figure 5: Refining value of $Mg(OH)_2$ and NaOH bleached pulps

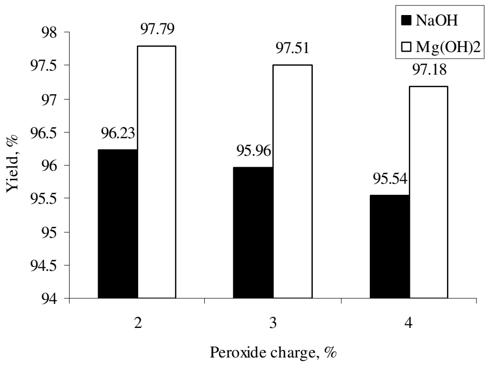

Figure 6: Pulp yield of $Mg(OH)_2$ and NaOH processes

Table 7
Properties of the bleaching effluent in the second phase

Process type	NaOH-process			$Mg(OH)_2$-process		
Treatment code	A	B	C	D	E	F
Residual H_2O_2 (%)	9.5	14.0	18.0	14.2	20.5	26.5
COD (kg/t)	43.5	54.3	69.9	27.3	29.6	31.8
E.C (ms/cm)	0.74	0.98	1.51	0.36	0.43	0.47

One of the main problems in alkaline peroxide bleaching is the amount of organic material dissolved under the alkaline conditions. Alkalization with magnesium hydroxide can be an alternative, as less lignanes and polyoses are dissolved.[3] The milder alkalinity of the $Mg(OH)_2$ system is believed to have many effects on pulp and bleaching process properties, such as the lower COD formation.

The COD load of the filtrate from the $Mg(OH)_2$-based bleaching was 37-55% lower than that from the NaOH process (Table 7). COD may come from dissolved carbohydrates, lignin, and other organic substances in the bleaching filtrate.[11] The decrease in COD indicates preserving of pulp yield and lowering of effluent clean-up requirements.[18] With a noticeable reduction in COD formation, the costs associated with effluent treatment would be significantly lower when using the $Mg(OH)_2$-based process.

This prediction was confirmed by the results obtained at a paper mill in Eastern Canada, which realized a 25-40% reduction in effluent treatment cost after implementing the $Mg(OH)_2$ peroxide bleaching process.[11] Also, the electrical conductivity (E.C.) values were very low in the $Mg(OH)_2$ system (Table 7), and remained constant at higher consumption levels of magnesium hydroxide. Less conductivity means less ionic trash in the paper machines, and lower retention aid requirements.[2]

The residual peroxide level in the $Mg(OH)_2$ process is very high, as compared to NaOH bleaching. There is a potential to recycle the peroxide in the post-bleaching filtrate back into the bleaching liquor;[18] therefore, the total peroxide consumption in the $Mg(OH)_2$ process would be lower than that of the conventional process.

CONCLUSION

In the first phase, the best ratio of alkali to peroxide was determined as 0.75. This alkali ratio in constant peroxide charge resulted in the highest brightness and the lowest yellowness and opacity of the bleached pulp. The bleaching selectivity factor reached its highest value at the 0.75 alkali ratio, upon a constant charge of NaOH.

In the second phase, the $Mg(OH)_2$ peroxide bleaching process produced bleached CMP with better yield and optical properties, and similar mechanical properties, in comparison with the NaOH peroxide bleaching process. However, the $Mg(OH)_2$-based process led to higher tear strength of the refined pulp samples, compared to the conventional process. The refining value (350 ml freeness) of the NaOH bleached pulp samples was lower than that of the $Mg(OH)_2$ bleached pulps. Also, the initial freeness of the NaOH bleached pulps was lower than that of the $Mg(OH)_2$ bleached pulps.

The greatest advantage of magnesium hydroxide over sodium hydroxide is its low chemical oxygen demand (COD), which means higher yield for the same reaction time and, in the case of hardwood pulp bleaching, an increase in bulk as well. At the different chemical charges of the $Mg(OH)_2$-based process, the residual peroxide is considerably greater than that resulting from the conventional process, indicating that the $Mg(OH)_2$ system has fewer peroxide decomposition reactions. $Mg(OH)_2$ prevents some of the hydroperoxide ion decomposition reactions, by releasing alkali more slowly, due to its low solubility.

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