Oxygen Delignification Technology for Improved product quality and pollution abatement in pulp and paper industry

Mukherjee, D. and Bandyopadhyay, N*

SUMMARY

The present article gives on overview of Oxygen Bleaching Technology in pulp and paper together with a brief introduction of conventional bleaching systems. Oxygen bleaching with respect to different consistencies and its chemistry are reviewed briefly. Use of oxygen in alkali extraction stage and effect of alkali, temperature, time and viscosity on delignification are discussed. Advantages of using oxygen in delignifying, pulp with respect to brightness, bleaching costs and stream pollution load are also discussed.

Man's earliest attempts to record human activities were made on stone[1]. After that, bark, leaves and ivory were also used. Between 2500 and 2000 BC the manufacture of a writing paper was started from a tall reed growing along the Nile called papyrus; hence the word paper. The actual manufacture of paper was invented by the Chinese about 105 AD. The industry obtained a strong foot hold in seventeenth century and in 1690 America's first paper mill was established[1]. Pulp manufacturing gradually developed into an industry of its own and served industries other than the paper industry as well. For example, the manufacture of pulp for rayon production has assumed major importance and become a distinctly specialized division of pulp manufacturing.

There is almost an exponential increase in pulp and paper production over the past nine decades. At the beginning of this century, the world's pulp production was only 12 million tons, where as currently it is about 100 million tons[2,3]. This enhanced growth can be accounted for by the demand for packaging materials, reading, writing as well as newsprint material. At present the leading pulp producers are the USA (50 million tons per year) followed by Japan (8 million tons per year).

This paper highlights the oxygen bleaching technology with respect to different consistencies, basic chemistry of oxygen bleaching and various parameters on delignification. Advantages of oxygen bleaching with respect to chemical savings, operational costs and pollution control are also highlighted.

Conventional Technology

Cellulose fibres obtained from different pulping processes are distinctly coloured. This colour depends on the original tree and the defibrating process applied. The colour ranges from dark brown for softwood kraft to creamish white for hardwood sulfite pulp. Bags, cardboard boxes and other types of coarse papers are manufactured from unbleached pulp. Bleached pulp finds applications where white or dyed paper is used. The origin of the colour in unbleached pulp is not yet fully understood. Cellulose and hemicellulose are inherently white. So they do not contribute to colour. Only on treatment with alkali under drastic conditions they are transformed to yellow compounds. Lignin

* Indian Oxygen Limited
Technology Centre
48/1, Diamond Harbour Road
Calcutta-700 027

(an amorphous high polymer of molecular weight about 40000) does not contribute to colour either, because its only absorption band lies at 280 mm. So, lignin has no colour effect on human eye. The only possibility is that during cooking, chromophoric and auxochromophoric complexes are formed from phenolic groups of the lignin molecule. These complexes cause light absorption in the visible spectrum.

The pulp has to be cooked or digested and sufficiently bleached in order to obtain a finished product of presentable appearance and good quality. By cooking and bleaching, one is able to remove the lignin from the carbohydrate portion of the pulp. Removal of lignin results in increased brightness of the product. Most pulping is done chemically either by the "Kraft" (using sodium hydroxide and sodium sulfide) process or "Sulfite" process (using sulfurous acid and bisulfite ions) with the former being more common.

Multistage bleaching is carried out normally in several stages using various chemicals and their combinations. But there are three basic steps. The first step is the dissolution of the ligneous compounds not eliminated during digestion of the wood. In the second step, fragmentized lignin is made soluble by alkali. The third step is an oxidation process applied to develop brightness. The most important bleaching stages and their abbreviations are listed below :—

Description	Symbol	Chemical used
Chlorination	C	Chlorine gas or Chlorine Water
Sequential Chlorine dioxide & Chlorine	D/C	Chlorine dioxide folowed by Chlorine
Mixture of Chlorine dioxide & Chlorine	C+D	Chlorine-Chlorine dioxide mixture
Sequential Chlorine and Chlorine dioxide	C/D	Chlorine followed by Chlorine dioxide
Alkali extraction	E	Sodium hydroxide solution
Chlorine dioxide	D	Aqueous solution of Chlorine dioxide
Peroxide	P	Hydrogen peroxide solution
Oxygen bleaching	O	Oxygen gas
Oxidative extraction	E/O	Oxygen in alkali extraction stage

A series of such stages is called a bleaching sequence. Average bleaching conditions for a Kraft pulp in CEDED sequence are shown in Table-1.

TABLE—1

Average Bleaching Conditions of Ceded Sequence

Reagent lb/ton air dried bleached pulp		Stock Consistency % air dried	Temp. °C	Relation Time hr	Final pH	Brightness/ Retention GE
Cl	120—180	3—4	Ambient	5—1	1—1.8	18—28
NaOH	40—60	10—12	60—70	1—2	9—11	—
ClO_2	10—20	12—14	70—75	3—4	3—4	75—85
NaOH	20—40	10—12	60—75	1—2	9—11	—
ClO_2	4—10	12—14	70—75	3—5	3—4	88—90

However, environmental pressure to reduce the overall effluent load from paper mills regarding air, water and solid discharges as well as to decrease the usage of chlorine containing chemicals has forced the industry to modify their pulping and bleaching techniques and to add new pollution abatement schemes,

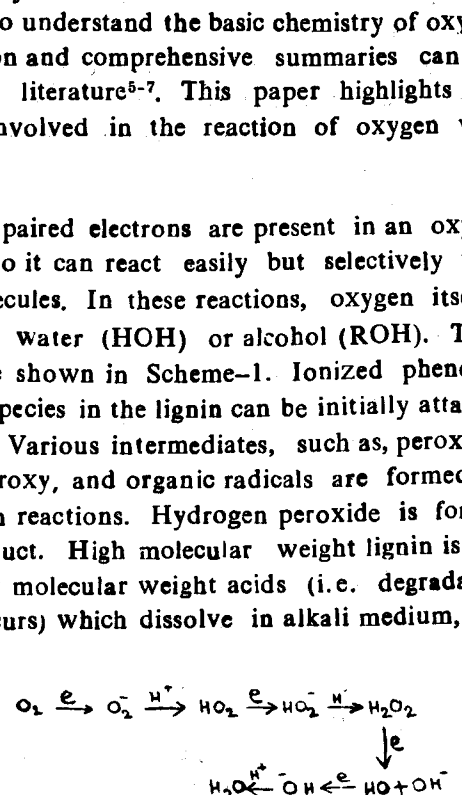
Oxygen Bleaching

Development of pulp and paper bleching using oxygen started in mid 1950s when Nikitin et al applied oxygen together with alkali for bleaching and refining of dissolving pulps[4]. In this process, cellulose degradation by oxygen led to substantial yield losses and inferior pulp strength. Later on, it was observed that magnesium compounds play a significant role in preserving the strength of the oxygen bleached pulp by inhibiting the carbohydrate degradation. This attributed to the key success of oxygen bleaching technoloy. Oxygen bleaching has been adopted mostly in the interest of environmental protection and commercial processes were developed in early 1970s. The incentive of the first oxygen bleach plants is to reduce the pollution load. Later on, other benefits, such as, lower operating costs and savings in bleaching chemicals in subsequent states have been realised.

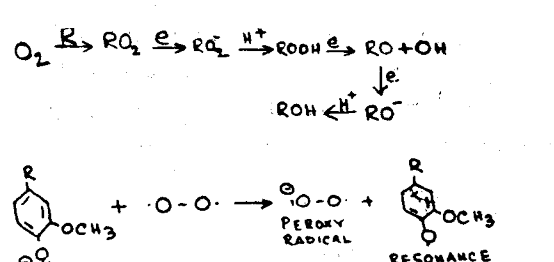
Chemistry of Oxygen Bleaching

Reaction mechanism involving oxygen and lignin is not yet fully established. Extensive research has been carried out to understand the basic chemistry of oxygen delignification and comprehensive summaries can be found in the literature[5-7]. This paper highlights the basic steps involved in the reaction of oxygen with lignin.

Two unpaired electrons are present in an oxygen molecule. So it can react easily but selectively with organic molecules. In these reactions, oxygen itself is reduced to water (HOH) or alcohol (ROH). These reactions are shown in Scheme–1. Ionized phenolate or enolate species in the lignin can be initially attacked by oxygen. Various intermediates, such as, peroxides, peroxy, hydroxy, and organic radicals are formed by radical chain reactions. Hydrogen peroxide is formed as a by-product. High molecular weight lignin is oxidised to low molecular weight acids (i.e. degradation of lignin occurs) which dissolve in alkali medium,



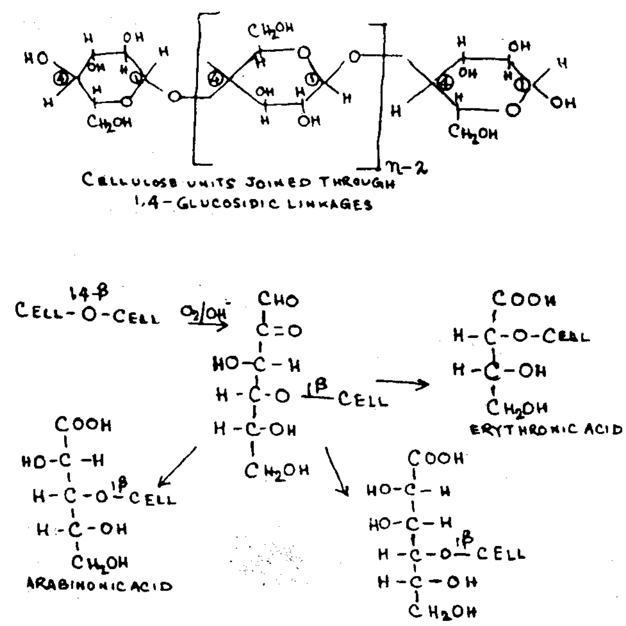
SCHEME-1 (Contd.)



SCHEME-1

The reactions of oxygen with lignin include inhibition of a phenolic hydroxyl group in the lignin to form a phenoate ion. This ion reacts with oxygen to form a reactive intermediate called a phenoxy radical which is stabilised by resonance. This intermediate then undergoes fragmentation whereby the polymer structure of lignin breaks up into fragments which are fairly soluble. Also hydrogen peroxide can further react with both the lignin and the carbohydrate portion of the pulp.

The intermediate radical formed are non selective oxidising agents. Hence, they can attack carbohydrate as well as lignin. Carbohydrate reactions occur mainly by the cleavage of chainlike cellulose molecules, Oxidative degradation of cellulose illustrated in Scheme-2. This cleavage of cellulose chains is believed to start with the formation of carbonyl groups in the chain thereby decreasing the chain length. Consequently, this results in lowering the pulp strength which is characterised by decrease in viscosity of the pulp. Such cellulose degradation is the major factor that limits the extent of delignification that can be achieved in the oxygen stage.



SCHEME-2

Most of the pulps contain iron, manganese and copper as impurities. It is observed that the rates of oxygen initiated free radical chain reactions (which result in extensive degradation of cellulose) are strongly influenced by these transition metal ions. This can be explained by their ability to decompose hydrogen peroxide and other organic peroxides to reactive species. One technique to inhibit such degradation is to remove the metal ions by acid washing prior to the oxygen stage. The other approach is to add magnesium compounds, called carbohydrate protector[8-11]. The inhibiting effect of magnesium compounds on cellulose degradation is due to deactivation of metal ion impurities. The metal ions are absorbed on precipitated magnesium hydroxide and their deleterious effect on peroxide is thereby eliminated. It should be mentioned here that mechanism of protection of cellulose from degradation by magnesium compounds is not completely understood.

Oxygen Bleaching Systems—

The solubility of oxygen in water (1 volume dissolves 0.03 volume O_2 at 20°C and 760 mm of Hg) is very low compared to that of chlorine (1 volume dissolves 2.26 volume Cl_2 under identical conditions). Consequently, oxygen, required for delignification must be transferred continuously to the reaction medium. Bleaching processes involving oxygen are usually mass transfer limited. In order to achieve efficient bleaching, oxygen must diffuse into the fibre by crossing the gas-liquid interface.

High Consistency System—

In high consistency system, water content in the pulp slurry is less. A large gas-liquid interfacial area is available. Also, the thickness of the liquid film through which the gas must diffuse into the fibre is decreased. Consequently, a higher rate of delignification can be obtained for higher consistency pulp.

Therefore, high consistency process for oxygen bleaching is most common and in use commercially[12,13]. Water is removed from the unbleached pulp to a consistency of 25-35%. The pulp is fluffed into the oxygen reactor after addition of magnesium ranging salt and alkali. The reaction is carried out at temperatures ranging from 90°—120°C at a pressure ranging from 612—1225 kPa for 20 to 60 minutes. The pulp is blown into the tank and subsequently sent to washers.

Advantages of High consistency process are good heat economy and improved pulp washing because of the dewatering unit used. Less amount of water is to be heated and the heat of reaction is almost enough to increase the temperature to the desired level.

However, the system suffers from the following disadvantages :

(a) high capital cost due to special equipment required for dewatering and handling of high density stock and pressure vessel;

(b) residual amounts of terpenes, carbon monoxide and volatile organic components (e g. acetone, methanol etc.) produced during oxidation from explosive mixtures with oxygen in a wide range of concentrations. Hence, provisions must be kept for safety systems to be installed.

Low Consistency System—

When the pulp consistency is low (about 2%), the liquid phase is sufficient to dissolve all the oxygen needed for delignification. Sufficient interfacial area between the aqueous pulp slurry and the gas is created by agitation. The rate of delignification is virtually the same at low and high consistency. This low consistency gives efficient mixing but has inherent disadvantages like higher steam requirement, larger reactor volume and handling of large quantities of liquid.

In late 1970, AIRCO has developed a unique low consistency bleaching system[14]. In essence, it is a pipeline reactor. It consists of a series of vertical falls and short horizontal lengths. The flowing slurry with proper velocity falls through an oxygen pocket and impinges onto the slurry in the lower portion of the conduit. This creates an intense turbulance necessary to dissolve the oxygen. Only one pump is required to move the slurry through a pipeline containing multiple mixing zones. One of the salient features of the fall device is the provision for addition of alkali at various locations along the reactor. This makes it possible to optimize the pH profile enabling upto 80% delignification without impairing the pulp strength. The system is suitable for retrofitting and the capital and operational costs are much lower than that for high consistency systems. The pipeline operates under pressure So there is no need to use a high pressure vessel like other delignification systemes.

Medium Consistency Systems—

With the advent of medium consistency technology it has been possible to mix oxygen effectively at a normal consistency of 8 to 15%. Otherwise conditions in medium consistency oxygen bleaching are more or less some as in high consistency bleaching.

In this process, the pulp, alkali and oxygen are fed at about 94°C to an upflow reactor. The residence time is typically 45 minutes and the reactor pressure is 420 kPa. Under these conditions, productions and brightness of the pulp is increased without affecting the strength of the pulp.

The medium consistency system offers following advantages over the high consistency system ;

(a) flexibility in layout and use of simpler equipment;

(b) lower steam requirement due to efficient use of blow heat;

(c) less corrosion due to lower consistency;

(d) lower capital cost;

(e) more lignin removal with less carbohydrate degradation;

(f) lower risk of explosion hazards caused by vapourised organic chemicals.

Due to above distinct advantages, the general trend in the pulp and paper industries is to shift towards medium consistency processes. Table-2 shows the operating data for high and medium consistency process[12].

TABLE—2

Operating Parameters for High and Medium Consistency Pulp

	High consistency	Medium consistency
Pulp consistency, %	25–28	10-12
Delignification, %	45–50	40–45
Retention time, min.	30	50–60
Initial temp °C	100–105	100–105
Pressure, kPa		
Inlet	500–600	700–800
Outlet	500–600	450–500
Power consumption, kw.h/ metric, ton	40–50	30–45
Steam consuption, Kg/metric ton		
Low pressure (450 kPa)	—	70
Medium prersure (1140 kPa)	75–100	200–300
Evaporator (450 kPa)	30–50	90–100
Alkali consumption, kg(metric ton	21–23	25-28
Oxygen consumption, kg/metric ton	20-24	20-24
Magnesium ion, kg/metric ton	0.5	0.5

Process Variables of the Oxygen Bleaching Stage—

Although the chemistry of oxygen bleaching is not yet fully understood, the oxygen bleaching technology is slowly being adopted by various industries abroad. Some studies of the effect of different process variables on bleaching performance have been published elsewhere[15]. The conditions for the oxygen stage and the most suitable sequence are predetermined by pulp requirements and mill's operating conditions.

The process variables in oxygen bleaching are oxygen and alkali charging, reaction time, temperature, use of magnesium complexes and consistency of the pulp. Oxygen charge must be sufficient otherwise incomplete bleaching would result. The bleaching or delignification is controlled primarily by alkali charge. This is illustrated in Fig. 1. It is observed that delignification process becomes very slow if the pH of the medium is less than 10. The reaction becomes faster

Effect of Alkali on Delignification

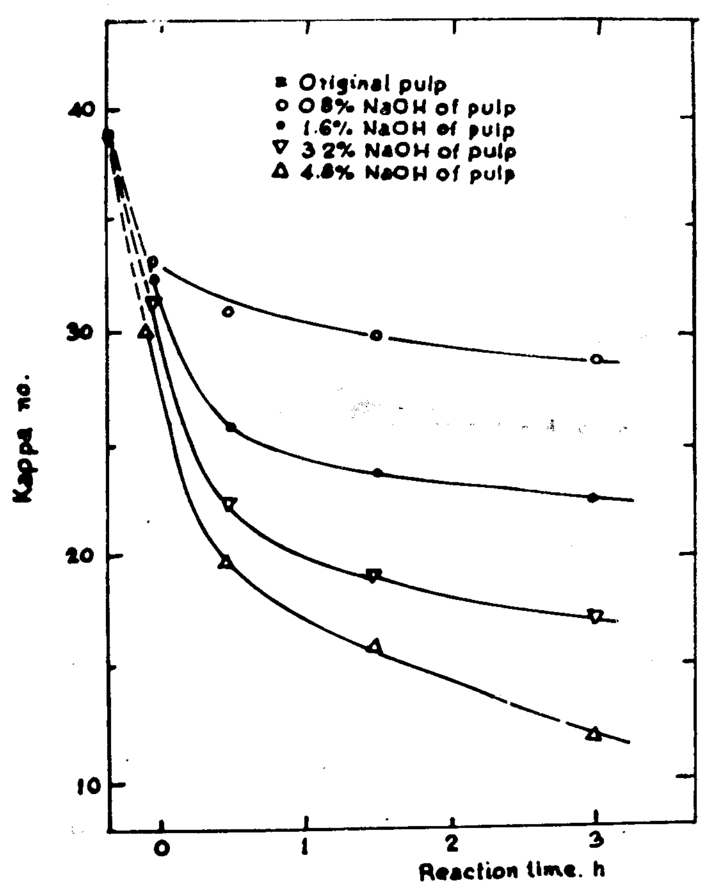


Figure 1

with increase in temperature. However, above 100°C the influence of temperature on Kappa number reduction is insignificant as shown in Fig 2

Influence of Temperature and Time on Kappa Number of Oxygen Bleached Pulp

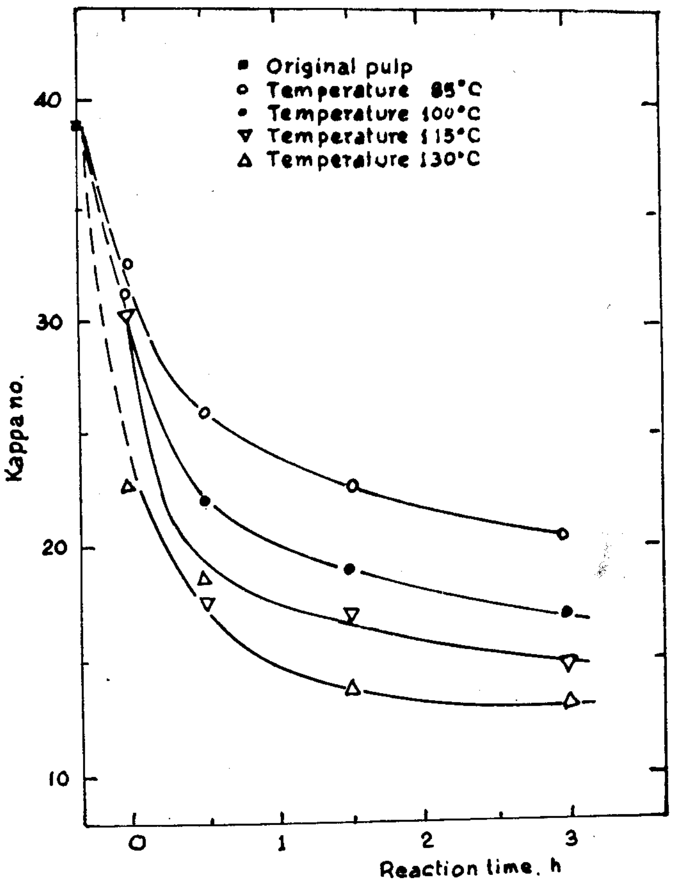


Fig. 2 (a)

Effect of Increased Temperature and Time on Delignification at Two Different Concentrations of Alkali

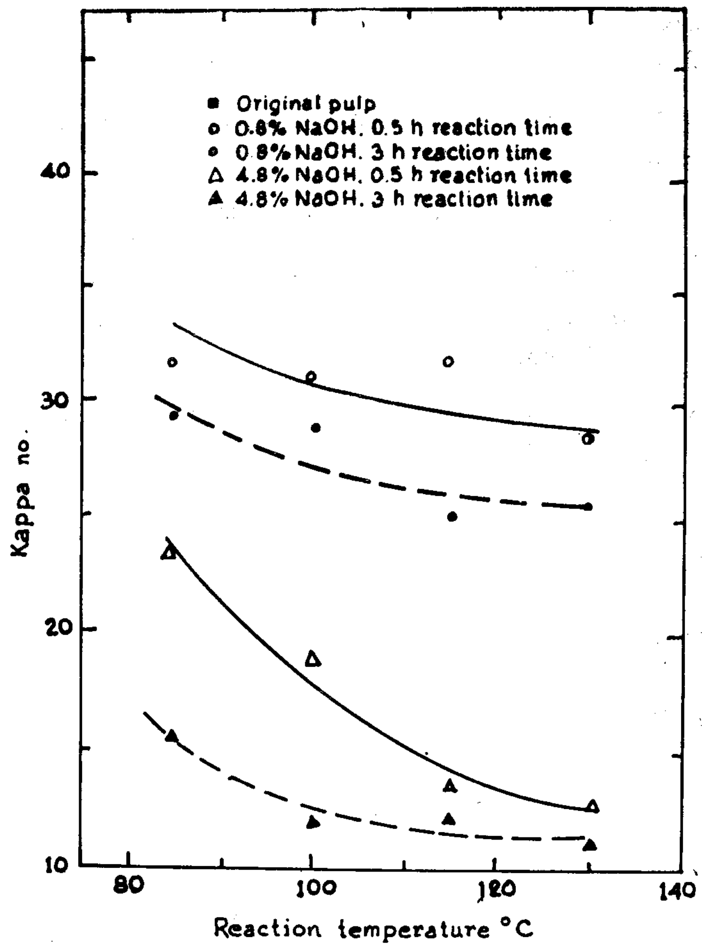


Figure 2(b)

Viscosity is a parameter which puts a limit on the extent of delignification. Cellulose degradation is characterized by drop in viscosity. Hence, relationship between viscosity and Kappa number is extremely important in oxygen delignification as shown in Fig. 3.

The rate of delignification is slower in medium than in high consistency bleaching. High pulp consistency contributes to more efficient contact between oxygen and pulp, eliminates the need for mechanical agi ation and lowers steam consumption. A reaction time of 30 to 60 minutes is required for high consistency under normal operating conditions whereas a reaction time of 90 minutes is required for medium consistency pulp. Typical conditions for medium consistency oxygen bleaching are shown in Table 3.

Oxidative Extraction, E/O

Oxidative extraction is carried out to dissolve coloured compounds made soluble by chlorine bleaching stage and to remove residual lignin. The use of an oxidative extraction stage in a bleaching sequence has gained rapid acceptance in commercial practice because it improves the bleaching efficiency and is fairly straightforward to implement[16,17]. Other advantages are low capital cost and reduced bleaching chemical costs. The most evident benefit in pulp quality is the increased brightness.

Lachenal et al[18] studied the influence of temperature, alkali charge and residence time on E/O performance He observed that temperature has a major effect on delignification provided enough alkali, was

Relationship Between Viscosity and Kappa Number of Oxygen Bleached Pulp

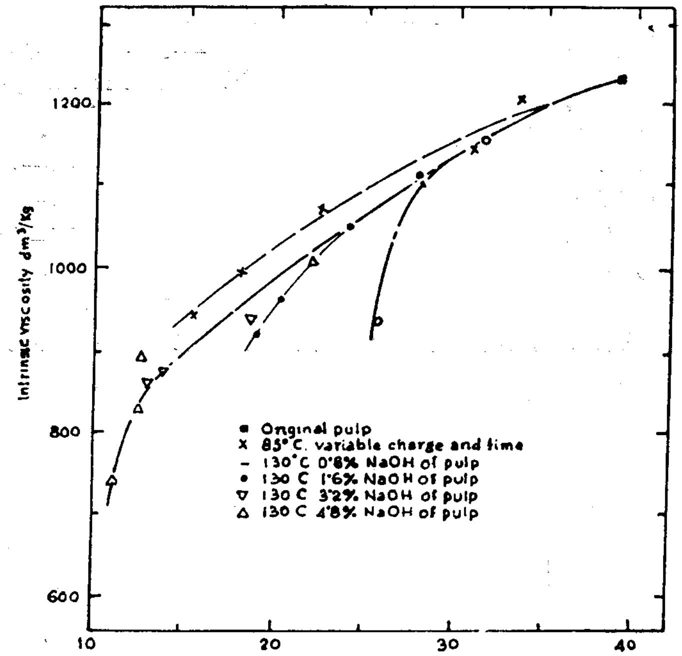


Figure 3

TABEL—3

Conditions in Medium Consistency Oxygen Bleaching

Kappa number reduction	from 32 to 18-20
Viscosity loss	max 200 cm³/gm
Yield loss	3·5— 4%
Consistency	10—14%
Temperature	90—100°C
Time	90 min
Oxygen consumption	20-22 kg/ADT
Alkali consumption	20-22 kg/ADT

added to the pulp at the start. E/O is normally carried out at temperatures above 50°C and pressure above 20 psig. Usually, the total retention time is 80 minutes. the O_2 pressure is 30 psig and the reaction temperature is 90°C. The alkali charge is 3% when delignification upto 30% can be achieved. Pulp consistency usually has no influence on the performance of the E/O systems but the most practical range is 9-14%.

Bleaching Sequences

Complete delignification of a pulp by means of oxygen and alkali would lead to severe deterioration in yield and strength of the pulp. Therefore other bleaching stages musts be used to complement the beneficial effect of the oxygen stage. The oxygen bleaching sequence will depend, among other things, on the unbleached Kappa number, final brightness and viscosity As the demand on viscosity and brightness is diminished, it is possible to extend delignification in the oxygen stage and consequently reduce the requirements for other bleaching chemicals. A few conventional and oxygen bleaching sequences are CEHDED, CEDED, CODED, OCEDED, ODED etc.

Bleaching Costs

On the basis of brightness ranging from 90-92% and viscosities over 900 cm³/g, the chemical requirements for conventional and oxygen bleaching sequences are discussed below. Fig. 4 gives the cost versus brightness plot. From Fig. 4 it can be concluded that a conventional bleaching sequence is more costly than oxygen bleaching sequence. Moreover, it is observed that the bleaching sequence OCDE/OD, where oxygen is used in two stages, is the cheapest one.

Comparative Chemical Costs for bleaching to 90% Brightness

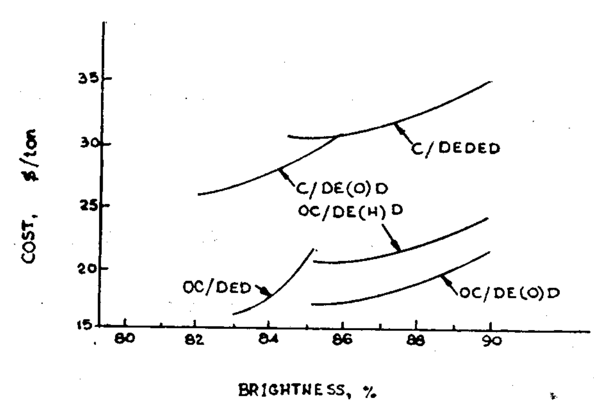


Figure 4

From Fig. 5 it can be concluded that the chlorine charge required by a CODED sequence is 75% of that using a CEDED sequence for a brightness of 92%. The chloringe charge is further reduced to 40% for a OCDEDED sequence compared to a CEDED sequence for same brightness. The corresponding figures for chlorine dioxide are 55% and 65%. Alkali requirements for oxygen bleaching schemes are higher but the net result is an appreciate savings in chemicals.

Chemical Costs Versus Brightness Comparison with conventional sequences

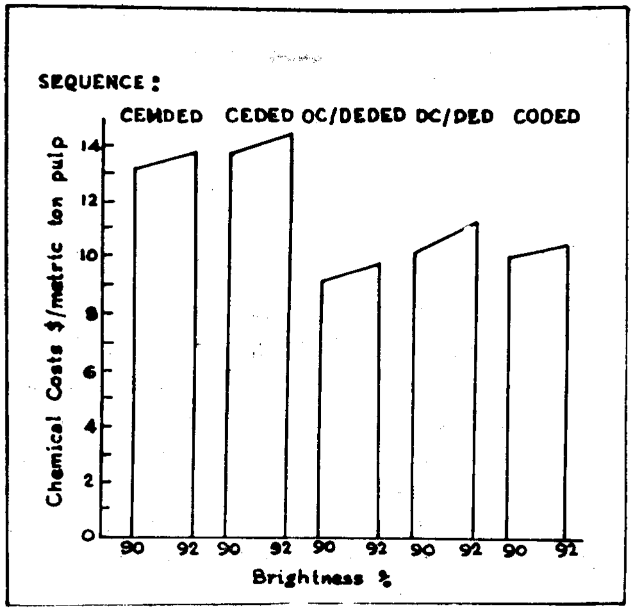


Fig. 5

Again when OCEDED is compared with CEHDED it is found that the former reduces the chlorine and the hypochlorite demand by 85 lbs and 25 lbs per ton of pulp.

Based on the relative costs and energy contents of the bleaching chemicals, a reduction of chemical costs of more than 25% can be achieved through the use of oxygen bleaching[19,20].

Brightness

Different brightnesses achieved with different oxygen sequences are tabulated in Table-4. Intrinsic viscosities are kept at around 915 cm^3/gm. The sequence ODED yields pulps having a brightness upto 85% with adequate viscosity and strength properties at reasonable cost. The very short sequence COD can achieve brightness in the range of 88-90% Fig 6 shows the relationship of viscosity to final brightness in OCEDED sequence and demonstrates that at target brightness of 92%, the viscosity does lie close to 900 cm^3/gm Thus it can be concluded that oxygen bleaching may be used in an OCEDED sequence to reach the required brightness and high viscosity. Table-4 also shows that a lower brightness, over 85%, can be easily achieved using an OCED sequence with very good viscosity.

TABLE—4

Brightness achieved for Different Oxygen Sequences—A Specific Viscosity

Sequence	Brightness (%) at Viscosity 915 cm^3/gm
OCED	86
COD	88—90
ODED	80—85
OC/DH	75—85
OCEH	70—80

Viscosity Versus Brightness for OCE DED Sequence

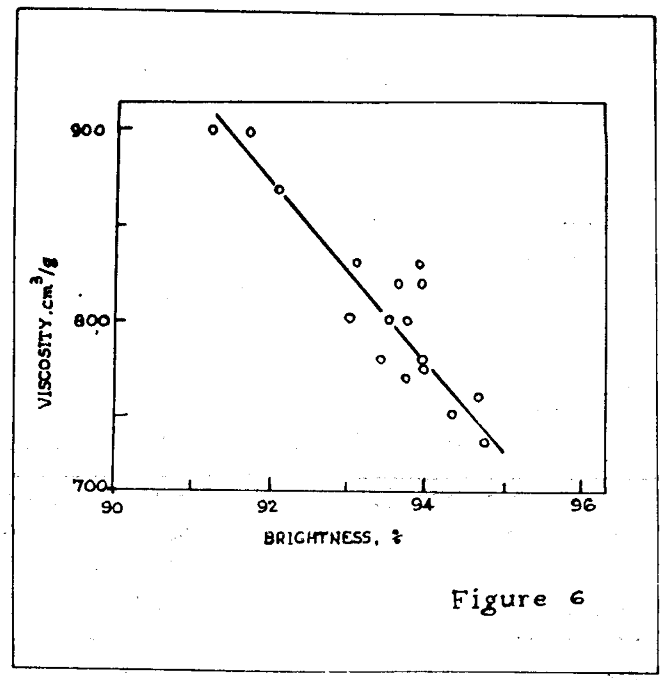


Figure 6

Pollution Abatement

The most significant benefit of oxygen bleaching technology is the reduction in effluent pollution load. Strong legislation aimed at virtual elimination of dioxin emissions has forced pulp mills to cut down the use of chlorine in favour of oxygen.

Tables-5A and 5B compare the significant reduction in effluent loading through oxygen bleaching as compared to conventional process. As shown in tables, a reduction of 94% in colour, 72% in BOD and 91% in chloride can be achieved through oxygen bleaching[21,22].

Also it is observed that partial replacement of chlorine with oxygen can significantly reduce the pollu-

Removal of Colour, Bod and Chloride Content Using an ODED Sequence

TABLE—5A

Stage	Colour lbs/ton	BOD lbs/ton	Chloride lbs/ton
C	79.5	18.3	44.4
E	89.5	6.7	8.3
D	2.3	1.0	2.6
E	7.6	2.6	0.0
D	5.7	0.9	2.8
	184.6	29.5	58.1

TABLE—5B

Stage	Colour lbs/ton	BOD lbs/ton	Chloride lbs/ton
O	Recycled	Recycled	None
D	2.3	2.5	2.7
E	6.4	3.5	0.0
D	2.3	2.3	2.7
	11.0	8.3	5.4
% reduction over Table-5A	94	72	91

tion load while complete replacement can reduce the effluent loading by as much as 75%.

Conclusion

Although oxygen bleaching is being used largely in Western Countries, the same will be adopted by Indian Pulp & Paper industries within next5 to 6 years.

It has been clearly demonstrated that introduction of oxygen in a particular bleaching sequence produces pulp of the same quality and yield as those obtained with conventional bleaching systems However, this can be achieved at a reduced cost with potentially lower effluent load. The oxygen stage in the system can be performed in presence of carbohydrate protecting Mg-complexes. This offers a unique way of reducing pollution from bleachery effluents. An additional advantage of oxygen bleaching is chemical savings. It can be further concluded that oxygen bleaching can reduce both capital and operating costs while producing good pulp quality.

Acknowledgement

The authors thankfully acknowledge BOC Group Technical Centre and AIRCO (a member of BOC Group) for providing valuable information.

References

1. Handbook of Pulp and Paper Technology, Reinhold, 1964, Britt (ed).
2. McDonough, T.J., Tappi Bleach Plant Operations Short Course, Hiltion Head, SC 1990.
3. Smook, G.A., "Handbook for Pulp and Paper Technologists," Tappi Press, Atlanta, GA 1990.
4. Nikitin V.M. and Akim, G.L., (i) Bumazh Prom 35, 5 (1960) (ii) Chem. Abstr. 53 (1959) 10757a.
5. Singh, R.P., 'The Bleaching of Pulp', Tappi Press, 3rd edition, 1979.
6. Kratzl, K., Gratzl, J. and Claus. P. AdV. Chem. Ser. 59 157 (1966).
7. Samuelson, O. and Stolpe, L., Tappi 52 1709 (1969).
8. Robert, A., Rerolle, P., Viallet, A. and Martin-Borret, O., ATIP Bulletin, 18 (4) 166 (1964).
9. Robert,A., Viallet,A., Rerolle, P. and Andreolety, J. P., ATIP Bulletin, 20 (5) 207 (1966).
10. Robert, A., Traynard, P. and Martin-Borret, O.
    (i) Can. Pat., 743, 847
    (ii) French Pat., 1, 387, 853
11. Rerolle, P. and Richard, C., French Pat., 1,404 605, May 22 1964.
12. Tench, L. and Harper, S., Tappi, 70 (11) 55 (1987)
13. Smith, K.E. Pulp and Paper, 56 (10) 90 (1982).
14. Kirk, Bradley S. and Kirschner Mark J., US Pat. 4,198,266 April 15, 1980.
15. Rerolle, P., Myburgh, H. and Robert, A, Pulp Paper Inter., 11 29 (1969).

16. Van Lierop, B., Liebergott, N., Teodoresen, G. and Kubes, G.J., Pulp Paper Sci., 12 (5) J133 (1986).

17. Enz, S.M. and Hallenbeck, M.R., Pulping Conference Proceedings, 1983, Tappi Press, Atlanta, p309.

18. Lachenal, D., Muguet, M. and Joly, P., Proceedings of Tappi Environmental Conference, Seattle, WA, 1990.

19. Waldestam, S., Jamieson, A. and Almberg, L., Pulp Paper, 54 (3) 92 (1980).

20. Croon, I. and Larssen, S., Pulp Paper Internat., 25 (1) 52 (1983).

21. Rowlandson, G., Tappi, 54 (6) 962 (1971).

22. Jamieson, A. and Smedman, L., Tappi, 56 (6) 107 (1973).