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OXYGEN BLEACHING PROCESSES: AN OVERVIEW

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ABSTRACT

This review surveys oxygen bleaching processes, including the established high-consistency processes and the developing medium- and low-consistency variants. Fundamental chemical and physical aspects common to all are first briefly considered, to provide a framework for descriptions of the processes and their behavior. Implications of the oxygen stage for the system as a whole are also outlined. A representative sampling of the literature is included.

INTRODUCTION

In 1867, the first patent on oxygen bleaching was issued (1,2). Commercialization was realized 103 years later. Although our industry is not noted for the speed with which it implements research results, most would agree that this is an extreme example of slow commercialization. The reasons for its slowness are instructive, in that they say something about how today's oxygen bleaching stages should be operated.

The process originally proposed involved mixing an alkaline pulp slurry with air at atmospheric pressure. The main problem with this approach was the poor solubility of oxygen in water. High oxygen pressure or extremely good mixing are needed to continually replenish the oxygen in the liquid phase as it reacts. When this was recognized, development work proceeded, but another serious problem remained - selectivity, the ability of the process to remove lignin without damaging the fiber.

Oxygen is an unusual molecule. It contains two unpaired electrons and thus has a natural tendency to react by forming free radicals. The selectivity problem arises from the extreme reactivity of the resulting radicals. Because of this, they tend to react with the first molecule they encounter, whether it be lignin or carbohydrate. Reactions with lignin stand a good chance of being productive, by depolymerizing it and making it soluble. Reactions with carbohydrate, on the other hand, usually result in chain breakage and, ultimately, loss of pulp strength. The discovery of the protective action of the magnesium ion in 1963 by Robert and co-workers (13) solved this problem and removed the last obstacle to the development of today's systems.

The driving forces for the development of oxygen bleaching are several. The principal one is environmental - substantial reductions in bleach plant effluent BOD and color are realized by removing about half of the lignin in the unbleached pulp in an oxygen stage before the chlorination stage. The dissolved material, unlike that from chlorination and caustic extraction, can be routed back to the recovery furnace, where it becomes a source of energy instead of a pollutant. Oxygen bleaching

contributes to an improved energy balance in other ways, too. The manufacture of oxygen requires only about one-eighth the energy required to make a chemically equivalent amount of chlorine. In addition, oxygen bleached pulps need less refining energy than conventionally bleached pulps. Still another advantage of oxygen-based sequences is that their chemical costs are less than for the corresponding conventional sequence (26). This is due to the oxygen being cheaper than the chlorine it replaces, the decreased requirement for caustic in the extraction stage and decreased chlorine dioxide consumption.

The environmental, energy-related and operating cost benefits of oxygen bleaching have combined to elevate it to the status of a significant new technological development. There are currently between 20 and 25 systems in operation producing a total of more than 13,000 tons of pulp per day.

FUNDAMENTAL ASPECTS

The chemistry of oxygen bleaching is quite complex, for two reasons. One is the variety of chemical structures present in the pulp. The other is the fact that oxygen may be transformed in the process to a number of different oxidizing species which differ in reactivity and the types of reaction which they are inclined to undergo.

Lignin Reactions

Model compound studies have established that important reactions of lignin are initiated when an ionized phenolic hydroxyl group reacts with oxygen. The product is a hydroperoxide, which will be ionized, to an extent which depends on the pH (7). The hydroperoxide is prone to fragmentation by a number of different pathways. Although these are not yet fully understood, they include side chain elimination, which breaks up the lignin macromolecule, and aromatic ring-opening reactions, which make the lignin fragments more water-soluble (6). The sequence of delignification reactions probably also involves the formation of phenoxy radicals, which may in a counterproductive step, react with each other to increase the molecular weight of lignin fragments, making them less soluble (7). A final important feature of the delignification process is that some of its component reactions produce hydrogen peroxide, which is capable of participating in further reactions with both lignin and carbohydrates.

Carbohydrate Reactions

Carbohydrate degradation is the main factor limiting the amount of delignification which can be achieved in the oxygen stage. It is manifested as a lowering of pulp viscosity and, if allowed to proceed far enough, as a reduction in pulp strength. It appears to involve free radical processes in which peroxides and metal ions play an important part (8-12)

In the presence of certain metal ions (e.g., Fe, Cu, Mn) hydrogen peroxide and organic peroxides catalytically decompose to very reactive radical species.

The resulting radicals can react with cellulose and hemicellulose in a number of ways. In one of

the most important, a hydroxyl group in one of the rings making up the cellulose chain is oxidized to a carbonyl group, and the chain is broken at that point by a beta-elimination reaction. In simpler terms, a ring containing a carbonyl group represents a weak link which is readily broken in alkaline medium. This random chain cleavage reaction reduces the degree of polymerization, and thus the viscosity, of the cellulose. It has less effect on yield since the chain fragments created are seldom short enough to be soluble.

The main type of reaction contributing to pulp yield loss in alkaline media is the peeling reaction, in which the cellulose chain is progressively shortened by the loss of single glucose units from one end of the chain. Because the part lost is a single unit, it is small enough to be soluble and contributes to an observed reduction in yield. The mechanism of the peeling reaction is similar to that of random chain cleavage in that both represent breakage at a weak point in the chain, the weakness being associated with the presence of a carbonyl group. In random cleavage, the carbonyl group is introduced by oxidation, whereas in peeling it is already there as the terminal aldehyde group at the reducing end of the molecule.

When a glucose unit is lost from the end of the chain by peeling, a new reducing end group is created. Since this new group is also subject to peeling, the process could conceivably continue until all the pulp dissolved. Fortunately, a competing process called the stopping reaction puts a stable (nonreducing) metasaccharinic acid group at the end of the chain, and no further peeling is possible.

In the oxygen bleaching of kraft pulps, yield loss is not a serious problem for two reasons. One is that the pulp has previously been subjected to a severe alkaline environment in the digester, and the stopping reaction has endowed the cellulose with a high content of stable end groups. The other is that oxygen itself converts reducing end groups to stable oxidized forms. It should be noted, however, that peeling can be a problem if random chain cleavage is excessive, since the latter reaction creates a reducing end group.

Selectivity and Protectors

Selectivity can be loosely defined as the ratio of attack on lignin to attack on carbohydrate. The latter can be described in terms of pulp viscosity or pulp yield to give two different measures of selectivity. They are commonly given in the form of plots of viscosity and yield against lignin content expressed as kappa number. For the reasons given above, viscosity selectivity usually receives more attention in the bleaching of kraft pulps.

The dominant factor governing selectivity in oxygen bleaching is the transition metal ion content of the pulp, since these ions catalyze the generation of harmful radical species. Most pulps contain appreciable quantities of iron, copper and manganese, all of which have this effect. One approach to dealing with the problem is to remove the metals by acid washing prior to the oxygen stage. Another is to add compounds to the pulp which inhibit

carbohydrate degradation. Such compounds may be referred to as carbohydrate protectors.

The protector of greatest commercial importance is the magnesium ion. The discovery of its effectiveness in 1963 by Robert and co-workers (13) provided a great impetus to the development of oxygen bleaching. Since then a considerable number of compounds have been found effective, but none is as economical as magnesium. It is normally applied at levels as low as 0.05-0.1% (o.d. pulp basis). It is believed to function by precipitating as magnesium hydroxide, which adsorbs the metal ions making them unavailable for catalysis of peroxide decomposition (14).

Figure 1 (26) illustrates the effectiveness of magnesium in preserving pulp viscosity and is typical of selectivities obtained in the bleaching of softwood kraft pulp.

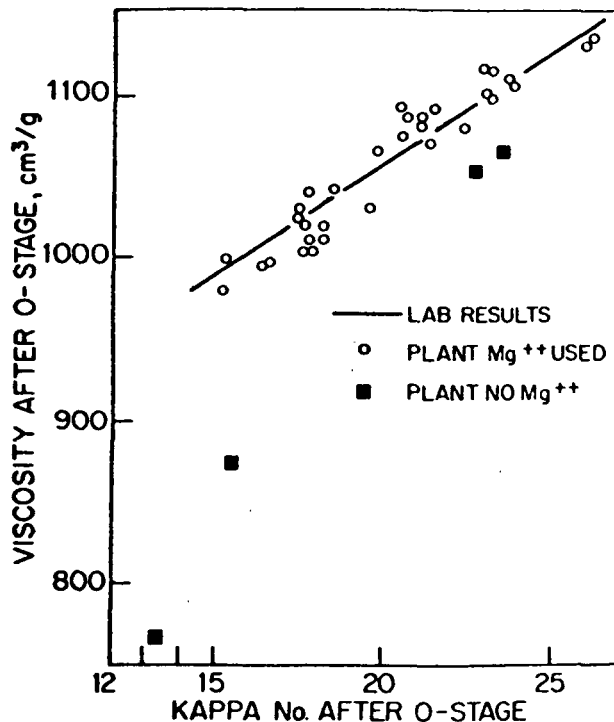


Fig. 1 Effect of magnesium ion on selectivity in the oxygen bleaching of Scandinavian softwood kraft (26).

Process Fundamentals

The intelligent design or selection of an oxygen bleaching process demands that adequate consideration be given to a number of its fundamental aspects. These include the relevant mass transfer phenomena as well as stoichiometric, kinetic, and thermodynamic aspects of the process. Mass transfer must be considered because we are dealing with a three-phase system. Oxygen must cross the gas-liquid interface, diffuse through the liquid film surrounding the fiber, and finally diffuse into the fiber wall before reacting. Kinetic studies carried

out under conditions of high oxygen availability in the liquid phase reveal the existence of an initial rapid delignification followed by a slower residual delignification (15,16). Both, but especially the first, may be diffusion rate-limited.

A potential difficulty is presented by the low solubility of oxygen in aqueous sodium hydroxide (17,18). Typically, bleaching at 15% consistency consumes 24 times as much oxygen as can be present in the liquid phase at any one time, and at 27% consistency, 50 times as much. A viable process must obviously facilitate the transfer of oxygen into and through the liquid phase. This can be done by ensuring that the partial pressure of oxygen in the gas phase and the gas-liquid interfacial area are both sufficiently large.

The question of how the rates of the delignification and carbohydrate degradation reactions depend on process variables has been addressed in several kinetic studies, including those referred to above (15,16). The general picture that emerges is that the lignin in the pulp appears to be of two different types which differ with respect to the ease of their removal by oxygen. The first type is removed within about the first 10 minutes in a rapid initial phase. Removal of the second type then proceeds according to a normal first order rate law, which means that the lignin content can be reduced to any desired level by allowing the reaction to continue for a long enough time. In practice, this is not normally observed because the extent of reaction is limited by the availability of alkali. The rates of removal of both types of lignin increase with increases in alkali concentration, oxygen partial pressure and temperature, but the sensitivity of the rate to all of these variables is less in the rapid initial phase. Interpretation of the kinetic data is complicated by the interesting observation that the amount of easily removed lignin depends on the reaction conditions.

Thermal effects are also important. At reasonable alkali levels, temperatures in the range 100-130° are needed, and consideration must be given to adding and recycling the required amount of heat, especially in the low-consistency processes. The heat of reaction is appreciable (19) and its removal may be a problem in high-consistency, high kappa-drop systems.

The stoichiometry of oxygen bleaching is such that, for each unit of kappa number reduction, about 0.10-0.13% NaOH (o.d. pulp basis) and a similar amount of oxygen are required. Reaction products include organic acids and carbon dioxide, small amounts of carbon monoxide, and traces of methanol. Since the last two are combustible, it is necessary to provide for control of their concentrations in the gas phase for safety reasons (21).

PROCESSES

Since the first commercial oxygen stage was started up in South Africa in 1970, considerable development of the process has occurred. A number of variants have emerged, the principal difference between them being the consistency in the reactor.

High Consistency Processes

One approach to solving the three-phase mass-transfer problem already described is to remove most of the free liquid phase. This has the twofold effect of providing very large gas-liquid interfacial areas and reducing the thickness of the liquid layer through which oxygen must diffuse to reach the fiber. Also, the amount of recycled potentially oxidizable, dissolved organic material in the reactor is reduced, as is the amount of water which needs to be heated to the reaction temperature.

For these reasons, most of the existing commercial installations operate at high consistency. Two systems are available: the Sapoxal process, marketed by Kamy, and the MoDo-CIL process, marketed by MoDo-Chemetics. The two are fairly similar, the only major difference being in the design of the reactor itself.

The MoDo-CIL process (22-26) uses a reactor designed to contain a continuous pulp bed at a consistency of about 27%, as shown in Fig. 2 (25). A potential problem with such an arrangement is bed compaction and the associated loss of free volume for oxygen to occupy near the bottom of the bed. However, this does not appear to be a real problem at consistencies as high as 27%. Feeding is by a screw feeder or thick stock pump which maintains a seal against the reactor pressure. At the bottom of the reactor the pulp is diluted to 5% consistency with recycled oxygen stage filtrate. Discharge is accomplished by a rotating cone equipped with screw threads and agitating arms.

The system is exemplified by those in operation at Eddy Forest Products in Espanola, Ont. and at the Franklin, Va. mill of Union Camp Corp. (22). The Eddy installation is shown schematically in Fig. 3 (24). Washed unbleached pulp is dewatered to a consistency of about 30% in a twin roll press or a screw press. Magnesium sulfate, alkali and steam are then added, and the pulp is fed to the reactor. White liquor is normally used as the alkali source for reasons of economy and to maintain the mill's sodium and sulfur balances. It must, however, first be oxidized since the sulfide ion would otherwise lead to a loss of selectivity in the oxygen stage. This is accomplished by contacting air or oxygen with the liquor in a separate vessel. Steam may or may not be added to the reactor itself, depending on the extent of delignification (and corresponding heat of reaction) and the retention time available. A typical set of conditions within the reactor would include: pressure 90 psig (80% oxygen) and temperature 110°C at a retention time of 30 min. Upon entering the reactor, the pulp passes through a fluffing mechanism and falls onto the bed. The bed level is sensed by a nuclear gauge and is controlled by changing the flow rate of the leaving stream.

In the high-consistency systems, the possibility of ignition of combustible gases represents a potential hazard. This is not a significant liability, however, since the possibility is removed by taking simple precautions. Concentrations of carbon monoxide, methanol and turpentine in the reactor must be monitored, and care must be taken to ensure that volatile additives (e.g., some defoamers) do

not enter the reactor with the pulp. The usual safety devices include an automatic relief valve, rupture discs and temperature - controlled quench showers. The concentration of combustible gases is controlled, usually by maintaining a continuous bleed stream. At least one installation (23) is equipped with a catalytic system for carbon monoxide destruction, which obviates the need for a bleed stream.

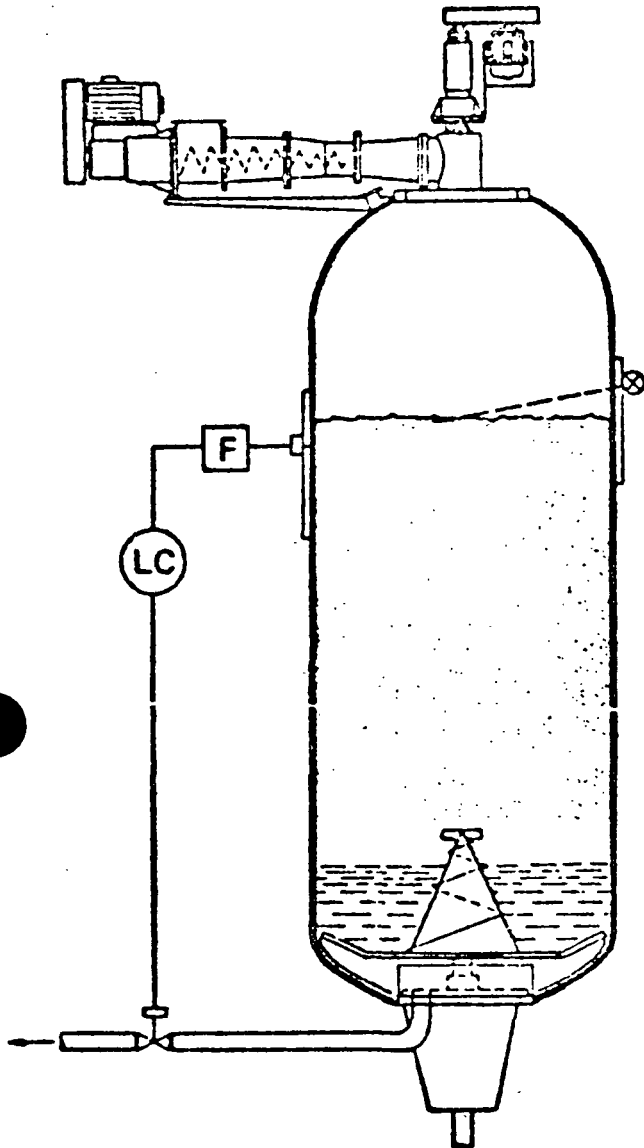


Fig. 2 Reactor used for the MoDo-CIL process (25).

The Sapoxal process (27-30) is inherently similar to the MoDo-CIL process, but operates at somewhat lower consistencies (17-25%), for which the reactor is especially designed. As illustrated in Fig. 4, it contains a series of trays, arranged one above the other. Each tray is divided into twelve compartments by radial walls and each has a cutout which coincides with the cross-section of the compartments. The trays, but not the walls, rotate, with the result that each compartment is emptied into the one below, once per revolution. The reten-

tion time of the pulp can thus be varied by varying the speed of rotation and is, within limits, independent of the production rate. Bed compaction, which tends to become more pronounced as the consistency is decreased, is avoided, since the bed depth is never greater than the distance between trays.

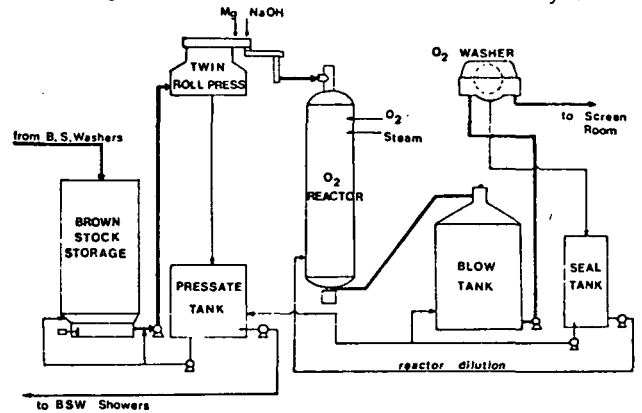


Fig. 3 Typical oxygen bleaching system (24).

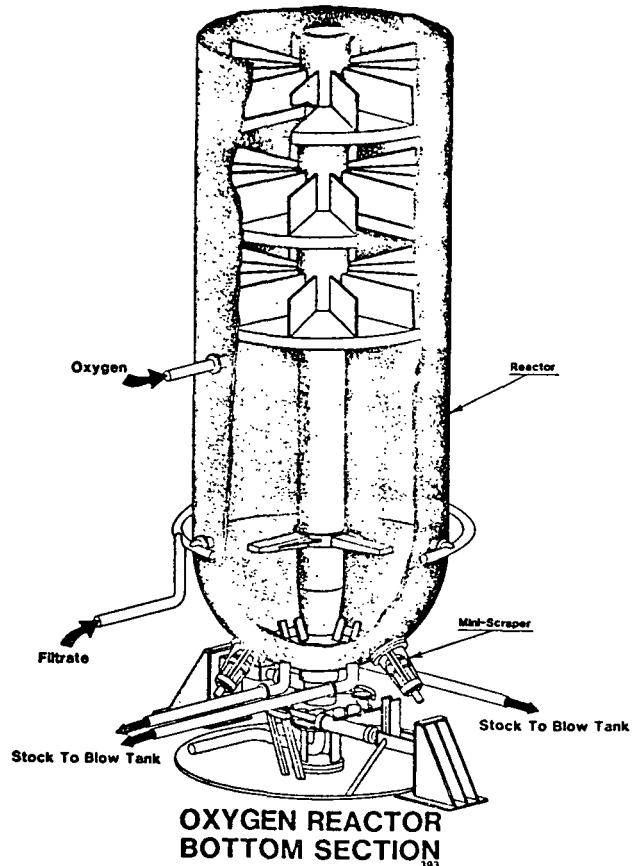


Fig. 4 Bottom section of reactor used for the Sapoxal process (Kamy, Inc.).

Advantages claimed for operating at the lower consistencies which this arrangement permits are lower bed combustibility and a lowering of the temperature rise associated with the reaction exotherm. Other advantages claimed are better control of retention time due to the absence of channelling, and

a more uniform gaseous atmosphere. It is apparently possible to operate these reactors without a gaseous bleed stream for combustible gas removal.

Low-Consistency Processes

At the other end of the spectrum of operating consistencies are the low-consistency processes (18,19, 31-35). Decreasing the consistency to 1% provides sufficient liquid phase to dissolve all of the oxygen required for typical degrees of delignification. A process based solely on such a two-phase system would, however, require a very large reactor and would have a severe liquid phase mass-transfer problem. The alternative which has been adopted is to create a pseudo two-phase system by finely dispersing oxygen in the liquid phase of pulp at somewhat higher consistency (3-5%).

International Paper Co. has developed such a system, which consists essentially of a high-shear mixer and a downstream conventional chlorination tower (33,34). A small pressurized preretention vessel is optionally placed between the mixer and the tower. In the absence of the preretention vessel, pressure is provided only by the hydrostatic head of the pulp in the tower. The latter type of system is said to be capable of achieving 50% delignification of softwood kraft in a 95-foot tall tower with 0.1N NaOH and 60 min retention (34).

A system developed by Rauma Repola is similar but provides for a cascade of several stages, each consisting of a mixer and a pressurized reactor with 5 minutes retention (35). Repeated oxygen addition relaxes the requirement for the dispersion of a relatively large amount of oxygen at one time.

A novel low-consistency system developed by Airco, Inc., (32) is an outgrowth of that company's wastewater treatment technology. As shown in Fig. 5, the reactor is a long pipeline to which oxygen is added at several points. Dissolution and dispersion of the oxygen at each addition point is accomplished in a static mixing device which consists simply of a vertical section of the pipeline. A gas pocket forms in the upper part of the section, and liquid falling through it creates intense turbulence, dispersing the oxygen. An attractive feature of this arrangement is that alkali addition points can be placed along the pipeline to give a variety of pH profiles. Selectivity is improved by optimizing the pH profile.

All of these processes offer the possibility of reducing the capital cost of oxygen bleaching by eliminating the need for expensive dewatering equipment upstream of the reactor. Some of them use low-pressure reactors, which may also reduce the cost. Penalties are incurred, however, in terms of increased reactor volume, steam requirements and dissolved organics in the reactor, which can lead to increased oxygen consumption. All of these problems are alleviated to some extent by the compromise of operating at medium consistency.

Medium-Consistency Processes

Processes operating in the 8-16% consistency range have been described by Kamy (36), Black-Clawson (37) and Sunds (38). The Kamy and Sunds versions

are similar to the low-consistency processes in that they produce a fine dispersion of oxygen in the pulp by intensive mixing. The pulp is then transferred to a retention vessel in which the delignification reaction is allowed to continue. The dispersions tend to be more stable than at low consistency, and the buoyancy imparted by the trapped oxygen tends to alleviate the bed compaction problem encountered at higher consistency. No special dewatering equipment is needed to operate in the medium-consistency range.

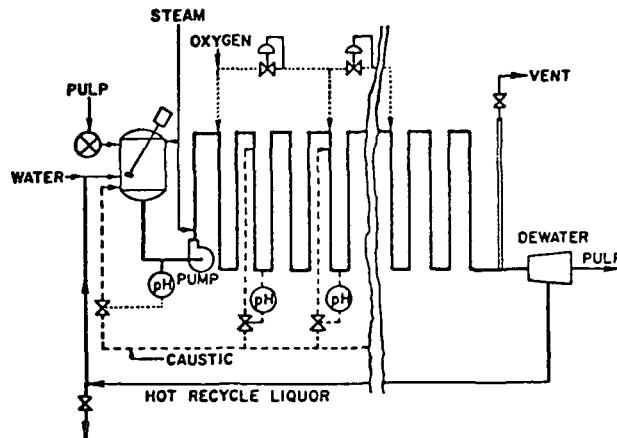


Fig. 5 Airco pipeline reactor system (32).

Possibly the best known of these processes is the one engineered by Kamy. It is in full operation at the M. Peterson and Søn mill in Moss, Norway, where it is used to lower the kappa number of 150 tons/day of polysulfide pulp from 60 to 30. It is shown schematically in Fig. 6. The unbleached pulp is diverted from a larger stream in a continuous digester blow line by a flow-splitting device which also acts as a coarse screen. It then passes through a unique in-line diffuser, which displaces residual black liquor with recycled oxygen stage filtrate, and subsequently to a mixer where oxygen is dispersed in it and alkali is added. The original mixer was a small disc refiner, but more efficient designs are now available. The reaction continues in a hydraulic reactor which, because it lacks a gas space above the pulp, is free from the hazards associated with combustible gas formation.

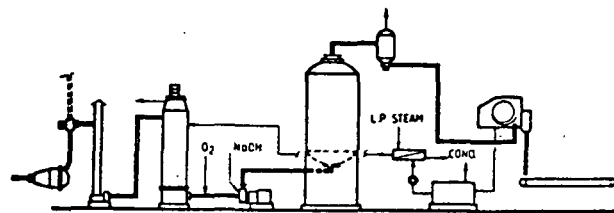


Fig. 6 Medium-consistency system at Moss, Norway (36).

The Black-Clawson process, developed in cooperation with Air Products and Chemicals (37), uses a Pandia digester. This consists of one or more horizontal tubes through which the pulp is transported by a screw conveyor. The atmosphere within the tubes consists largely of pressurized oxygen. The gas-liquid interface is continuously renewed as a result of the agitation provided by the screw

conveyor. As in the Airco low-consistency process, the pH profile can be controlled by addition of alkali to the tubes.

The medium-consistency processes are attracting increased attention, partly because of their potentially lower capital costs relative to the established high-consistency systems, and the small steam, chemical and reactor volume penalties they incur relative to those incurred by the low-consistency systems. It is also claimed that they are more selective than the high-consistency systems, but the magnitude of this effect has yet to be convincingly demonstrated.

Oxygen in the Extraction Stage

A recent finding is that addition of a relatively small amount of oxygen to an existing extraction stage can sharply reduce chlorine dioxide requirements in the later stages or allow full bleaching in only 3 stages (39,40). This is an attractive possibility, since the only capital outlay required for an existing bleach plant is for an oxygen mixer. This assumes that an upflow extraction tower is available to provide some pressurization in the form of hydrostatic head. Even if the extraction tower is of downflow design, the desired effect can be obtained merely by adding an upflow preretention tube. Swedish mill experience indicates that consumption of 4 kg oxygen saves 8-9 kg active chlorine in the form of chlorine dioxide (39).

A related development is displacement bleaching with oxygen. This has been demonstrated recently at the Ahlström mill in Varkaus, Finland (41). Oxygen was dispersed in the E₁-stage liquor, which was then passed through the pulp bed in the displacement bleaching tower. Significant ClO₂ savings were realized in the subsequent stages.

PROCESS VARIABLES

The response of the oxygen bleaching system to changes in process variables is a manifestation of the kinetics of the component chemical reactions and mass-transfer processes. Kinetic studies such as that of Olm and Teder (15) therefore provide a useful framework for predicting these effects and rationalizing observations such as those made by Hartler et al. in their process variable studies (42).

Time and Temperature

At fixed alkali concentration, the decrease of kappa number with time exhibits two distinct phases, both of which are first order rate processes. As illustrated in Fig. 7 (15), there is an initial rapid drop followed by a slower one. This is interpreted as being due to the presence of two types of lignin which differ in ease of removal. The two delignification phases are directly paralleled by two corresponding cellulose depolymerization phases (Fig. 8).

A consequence of the first-order nature of the delignification process is that, given enough alkali, the kappa number will continue to drop indefinitely. This is in contrast to the normal observation that the process appears to stop when a

limiting kappa number is reached, as shown in Fig. 9 (3,42). The latter behavior results when the alkali charge is exhausted. Figure 9 also serves to show that delignification is considerably accelerated by an increase in temperature; the point of alkali exhaustion is reached much more rapidly at 130° than at 85°.

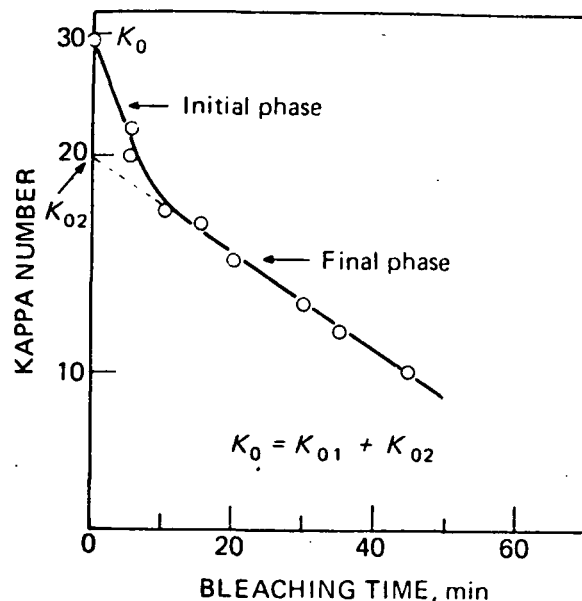


Fig. 7 Logarithm of lignin content vs. time at constant alkali concentration. Conditions: 110°C, 0.02M NaOH, 0.98 MPa (10 atm) O₂ pressure (15).

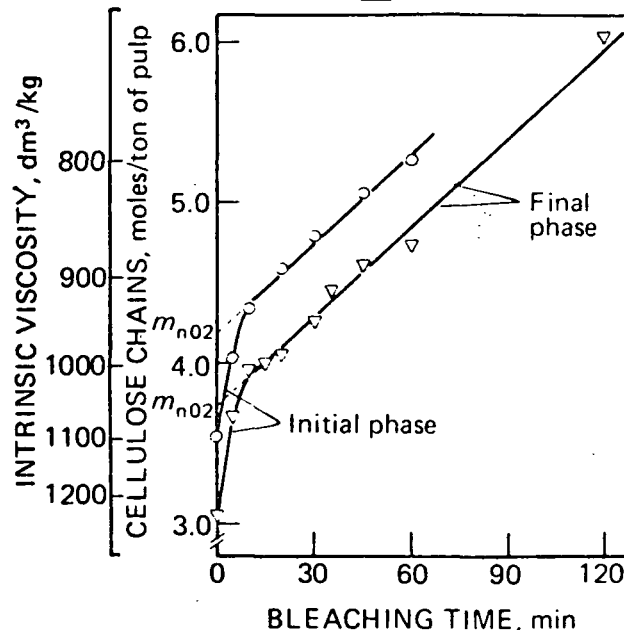


Fig. 8 Carbohydrate depolymerization in two different pulps at constant alkali concentration (15).

As shown in Fig. 1, the parallel between the rates of delignification and carbohydrate degradation results in a good correlation between viscos-

ity and kappa number. This relationship tends to be fairly independent of process variables, although it does get steeper at higher temperatures and also falls off at prolonged reaction times in the absence of residual alkali.

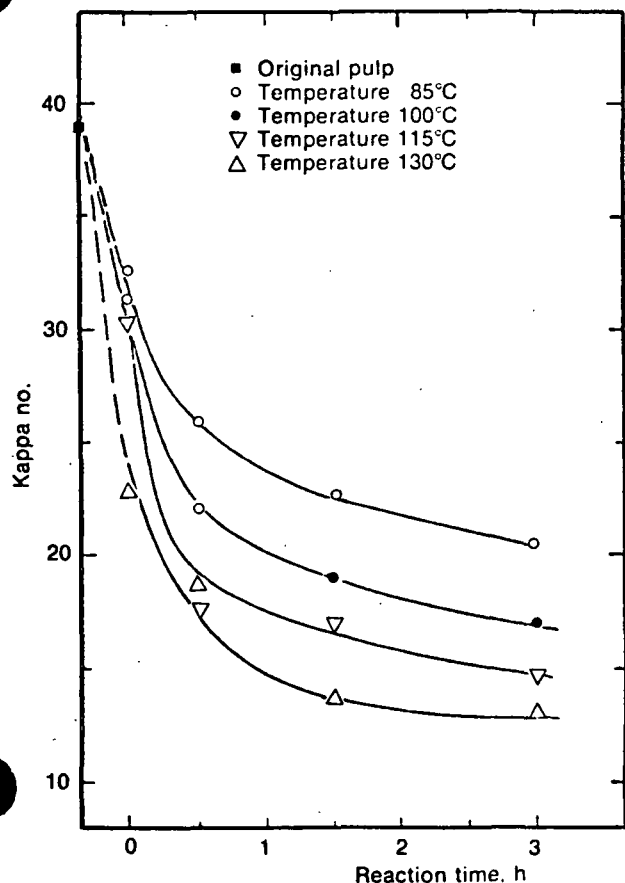


Fig. 9 Effect of temperature on oxygen delignification rate. Conditions: 3.2% NaOH (o.d. pulp basis), 5 atm total pressure, 20% consistency (3,42).

Alkali Charge

Both delignification and cellulose degradation are substantially accelerated by increased alkali concentration and therefore by increased alkali charge at constant consistency. The increase in delignification rate is illustrated by Fig. 10 (3,42).

Oxygen Pressure

In general, the effect of oxygen pressure (2-15 atm) is small in comparison to the effects of alkali charge and temperature (42). However, it must be remembered that a given system may be either chemical reaction rate controlled (as in well-stirred, slowly reacting systems) or mass-transfer rate controlled (as in poorly mixed, fast-reacting systems). Oxygen pressure is expected to have a greater effect in systems of the latter type. Higher pressures accelerate both the delignification and carbohydrate degradation reactions.

Consistency

In spite of its far-reaching process implications, the effect of consistency at fixed alkali charge is relatively small. Lowering the consistency results in a moderate slowing down of both the delignification and carbohydrate degradation reactions, as a result of the associated decrease in alkali concentration.

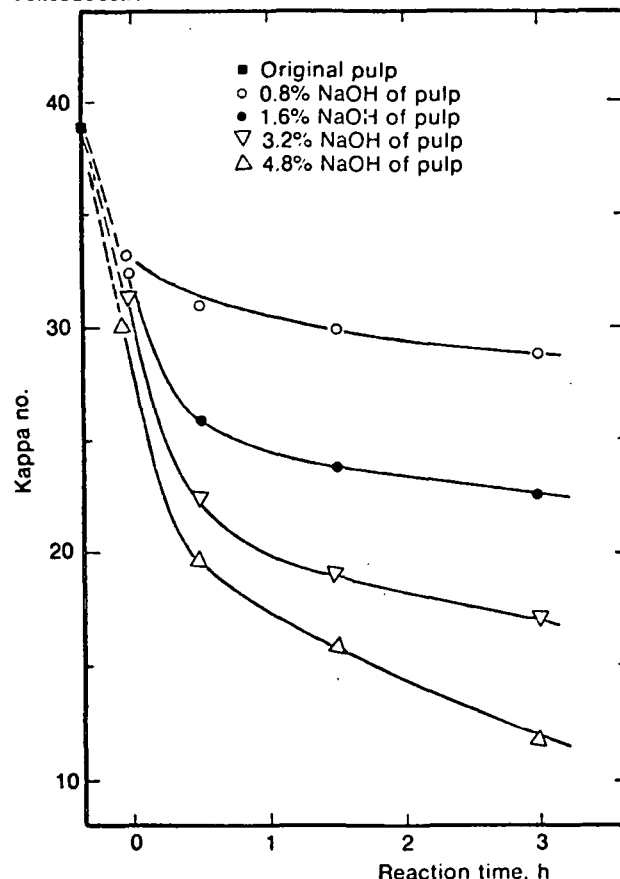


Fig. 10 Effect of alkali charge on delignification rate. Conditions: 100°C, 5 atm total pressure, 20% consistency (3,42).

SYSTEMS ASPECTS

Placement of the Oxygen Stage

If an oxygen stage is to be used for predelignification, it is most logically integrated into the brown stock washing system. Good upstream washing is essential, since black liquor solids both consume oxygen and damage selectivity. Good downstream washing is necessary to fully realize the pollution abatement potential of the stage. Oxygen stage washer filtrate is used as wash liquor in the brown stock system and thus finds its way back to the recovery system. Oxygen stage washer losses enter the chlorination stage and become unrecoverable.

Placing the oxygen stage in the brown stock washing area necessitates closing the screen room water circuit to avoid the loss of oxygen stage solids. Foaming problems normally dictate the use of pressure screens.

Oxygen predelignification is usually limited to removal of about 50% of the lignin in the unbleached pulp to avoid pulp strength loss. The subsequent chlorination stage would be conducted at high temperature because of the normally high temperature of the pulp leaving the oxygen stage washers. Addition of chlorine dioxide thus becomes necessary and the metallurgy of the chlorination washer must be appropriate.

Placement of the oxygen stage after the chlorination stage offers little in the way of pollution abatement benefits but makes short-sequence bleaching possible, as at Chesapeake (43). With the recent development of oxygen mixers, simple addition of oxygen to the extraction stage would have to be considered as a possible alternative.

Implications for the Recovery System (44)

If pure sodium hydroxide were used as alkali in the oxygen stage, the amount added, together with the ClO₂ generator spent acid, would probably exceed the requirement for sodium make-up to the liquor system. For this reason, oxidized white liquor is often used as an alkali source. If white liquor were used to satisfy the total alkali requirement of the oxygen stage, an increase of about 7% in the capacity of the causticizing and lime reburning systems would be needed.

The additional water added with the alkali and as direct steam in the oxygen stage amounts to about 0.4 lb/lb pulp. A corresponding increase in evaporator capacity would be required. Alternatively, washing capacity could be added to allow a corresponding decrease in the dilution factor.

Recycling of organic material dissolved in the oxygen stage to the recovery furnace typically increases the load on that unit by 3-5%.

SUMMARY

In the past fifteen years, after a long period of dormancy, oxygen bleaching has attained the status of a significant technological development. This came about as a result of the need for environmental improvement, the discovery of the protective action of magnesium ion, and the identification of appropriate operating conditions.

The problem of oxygen transfer within a three-phase system was first solved by removing most of the free liquid phase, giving rise to the high-consistency processes. These are now well-established but are about to be challenged by medium-consistency processes which offer potential capital cost advantages and which make use of recently introduced gas-liquid mixing technology.

Current research is leading to a better fundamental understanding of the behavior of oxygen bleaching systems. This knowledge may be expected to result in further improvements in the technology.

REFERENCES

General Review Articles

1. A. Robert and C. de Choudens, "Oxygen in the

Cellulose Pulp Industry, A.T.I.P. Rev., 36(6-7): 332(1982).

2. J. Bentvelzen, "Oxygen Bleaching Today - A Review." Proceedings of the Northwest Regional Conference of The Institute of Paper Chemistry, Seattle, WA, 1979.
3. R. P. Singh and B. C. Dillner, "Oxygen Bleaching," in "The Bleaching of Pulp," Tappi Press., Atlanta, GA, 1979, p. 159.
4. J. A. Garcia-Hortal, "Oxygen Bleaching of Kraft Pulp," Invest. Tech. Papel, 15(58): 933(1978). (Translation available from The Institute of Paper Chemistry),
5. I. Croon and D. H. Andrews, "Advances in Oxygen Bleaching I. Demonstration of Its Feasibility and Scope," Tappi, 54(11): 1893(1971).

Lignin Reactions

6. J. Gierer and F. Imsgard, "The Reactions of Lignins with Oxygen and Hydrogen Peroxide in Alkaline Media," Svensk Papperstid., 80: 510(1977).
7. M. R. San Clemente, K. V. Sarkanen, and S. E. Sundin, "Alkaline Autoxidation of 4-Ethylguaiacol," Svensk Papperstid. 84(3): R1(1981).

Carbohydrate Reactions

8. E. Sjöström, "The Chemistry of Oxygen Delignification," Paperi Puu, 63(6-7): 438(1981).
9. O. Samuelson, "Oxygen as Delignifying Agent," Svensk Papperstid., 83(8): 205(1980). (Translation available from The Institute of Paper Chemistry.)
10. Proceedings of the Symposium on the Chemistry of Delignification with Oxygen, Ozone, and Peroxides held at Raleigh, N.C., May 27-29, 1975. Uni, Tokyo, 1980.
11. O. Theander, "Carbohydrate Reactions in Oxygen-Alkali Delignification Processes," Ref. 10, p. 43.
12. E. Sjöström, "Behavior of Pulp Polysaccharides During Oxygen-Alkali Delignification," Ref. 10, p. 61.

Protectors

13. A. Robert, P. Traynard, and O. Martin-Borret, French Pat. 1,387,853(1963).
14. A. Robert and A. Viallet, A.T.I.P. Rev., 25: 237(1971).

Process Fundamentals

15. H. Olm and A. Teder, "The Kinetics of Oxygen Bleaching," Tappi, 62(12): 43(1979).
16. J. E. Evans, V. Venkatesh, J. S. Gratzl, and H. Chang, "The Kinetics of Low-Consistency

Oxygen Delignification," Tappi, 62(6): 37(1979).

17. A. Broden and R. Simonson, "Solubility of Oxygen. Part 2. Solubility of Oxygen in Sodium Hydrogen Carbonate and Sodium Hydroxide Solutions at Temperature < 150°C and Pressures < 5 MPa," Svensk Papperstid., 82(16): 487 (1979).
18. G. L. Akim, "Oxygen Bleaching at Different Consistencies," Paperi Puu, 63(4a): 291(1981).
19. R. Hillström, A. Jamieson, B. Lindqvist, and L. Smedman, "Process Concepts for Oxygen Delignification," Svensk Papperstid., 80(6): 167(1977).
20. Seminar Notes, 1978. "Oxygen, Ozone, and Peroxide Pulping and Bleaching Seminar Notes," Tappi, Atlanta, 1978.
21. J. D. Karna, G. K. Brock, and D. M. Shellhammer, "Safety in Oxygen Delignification Vessels" Ref. 20, p. 46.

High Consistency Processes

22. K. E. Smith, "Oxygen Bleaching System Operating Well at Union Camp's, Franklin Mill," Pulp Paper, 56(10): 90(1982).
23. L. Almborg, A. Jamieson, B. Andersson, and S. Noreus, "Two Swedish Mills Start up Oxygen Bleaching," Pulp Paper Can., 81(2): 80(1980).
24. J. H. Lund and C. R. Cook, "O₂ Delignification System is Successful at Eddy," Pulp Paper Can., 81(1): 49(1980).
25. A. G. Jamieson and L. A. Smedman, "Mill Scale Application of Oxygen Bleaching in Scandinavia," Tappi, 57(5): 134(1974).
26. A. Jamieson, S. Noreus, and B. Pettersson, "Advances in Oxygen Bleaching III. Oxygen Bleaching Pilot Plant Operation," Tappi, 54(11): 1903(1971).
27. J. E. Svensson, "Experiences of the Sapoxal Oxygen Bleaching System at Skutskar Mill, Sweden," Ref. 20, p. 54.
28. E. David, A. Cannone, J. Carles, and M. Durand, "Oxygen Bleaching - Two Years of Operating Experience in France," Pulp Paper International 18: 47(1976).
29. B. Coetzee, "Sapoxal Bleaching-Operating, Technical Experience," Pulp Paper Mag. Can., 75(6): T223(1974).
30. G. Rowlandson, "Oxygen Bleaching in Commercial Production," Tappi, 54(6): 962(1971).

Low-Consistency Processes

31. L. Almborg, A. Jamieson, and I. Croon, "Oxygen Delignification as Part of Future Mill Systems," Ref. 20, p. 27.

32. B. S. Kirk, M. J. Kirschner, and J. K. Tseng, "Low Consistency Oxygen Delignification in a Pipeline Reactor - A Pilot Study," Tappi Conference Papers/Alkaline Pulping/Secondary Fibers, 1977, Tappi, Atlanta, 1977; Tappi, 61(5): 77(1978).
33. K. J. Brown, P. J. Connery, T. R. Clarke, and R. B. Phillips, "Low-Consistency Oxygen Delignification. Part I - Process Concept," Ref. 20, p. 15.
34. S. K. Roymoulik and K. J. Brown, U.S. Pat. 3,832,276(Aug. 27, 1974).
35. I. A. Yrjala, L. J. Suoninen, and P. K. Paasonen, "New Aspects in Sulfate Pulp B leaching," Proceedings of the 1976 International Pulp Bleaching Conference, Tappi, Atlanta, 1976, p. 147.

Medium-Consistency Processes

36. P. J. Kleppe, P. C. Knutsen, and F. Jacobsen, "Oxygen/Alkali Delignification at Medium Consistency. Mill-Scale Trials to Commercial Installation," Tappi, 64(6): 87(1981).
37. E. F. Elton, V. L. Magnotta, R. D. Markham, and C. E. Courchene, "New Technology for Medium-Consistency Oxygen Bleaching," Tappi, 63(11): 79(1980).
38. G. Annergren and L. Näsman, "Medium Consistency Oxygen Bleaching - An Alternative to High Consistency Oxygen Bleaching?" Proceedings of the 1979 International Pulp Bleaching Conference, Toronto, 1979. p. 99.
39. G. Carré and G. Annergren, "Oxygen Alkali Extraction: A Versatile Tool Toward a Simplified Bleaching Technique." Proceedings of the 1982 International Pulp Bleaching Conference, Tappi, Atlanta, 1982, p. 17.
40. L. Lindstrom, S. Nordén, and G. Carré, "Bleaching of Softwood Kraft Pulp in a Short D/C-OE-D Sequence.
41. V. Kortelainen, J. Sipiläinen, B. Arhipainen, and J. Gullichsen, "Displacement Bleaching with a Gas Suspended in Liquor." Proceedings of the 1982 International Pulp Bleaching Conference, Tappi, Atlanta, 1982, p. 1.

Process Variables

42. N. Hartler, H. Norrström, and S. Rydin, "Oxygen Alkali Bleaching of Sulfate Pulp," Svensk Papperstid. 73(21): 696(1970).

Systems Aspects

43. Anon. "Integrated Use of Oxygen in Pulp and Papermaking." Chem. Eng., Nov. 24, 1975, p. 52.
44. SSVL (Swedish Forest Industry Foundation for Water and Air Protection, Environmental Care Project) Technical Summary, 1974.