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CHLORINATION

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CHLORINATION

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ABSTRACT

This paper describes the principles and application of pulp chlorination. Relevant aspects of the chemical reactions of chlorine with water, lignin and carbohydrates are first considered. The effects of changes in process variables are then examined, as a basis for discussion of the process and its components. Special attention is paid to stock dilution, dispersion, mixing and control.

INTRODUCTION

Kraft pulp bleaching sequences almost always begin with a chlorination stage and a subsequent caustic extraction stage. Their purpose is to remove the bulk of the lignin that remains after pulping. The resulting delignified pulp can then be treated in one or more brightening stages to further reduce the lignin content and oxidize the remaining traces to a colorless form.

Efficient chlorination is essential for the economical production of high quality bleached pulp. Inadequate chlorination increases total bleaching cost because the chemicals used in the brightening stages (usually chlorine dioxide) are more expensive than chlorine. On the other hand, excessive, poorly controlled, or inappropriate chlorination increases the risk of pulp degradation because chlorine tends to be less selective than chlorine dioxide.

The purpose of this paper is to provide the basic information required for an understanding of chlorination systems and the principles governing their sound operation.

PROCESS OVERVIEW

A typical chlorination flowsheet is shown in Fig. 1.

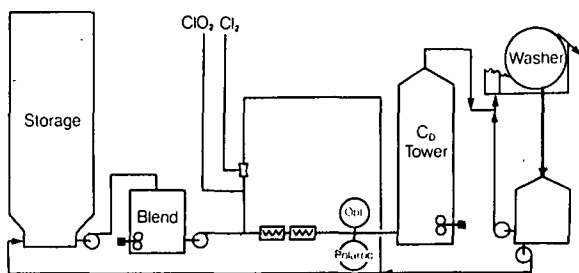


Figure 1. Chlorination process flowsheet.

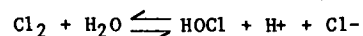
Screened, unbleached pulp is diluted with recycled chlorination washer filtrate and pumped to an agitated blend tank to smooth out variations in K no.

and consistency. Chlorine gas is dispersed as small bubbles in flowing water or filtrate, and, before the bubbles have time to coalesce, the dispersion is injected into the pulp suspension as it flows from the blend tank to a pair of static mixers. A small amount of chlorine dioxide is usually added with the chlorine to prevent excessive carbohydrate damage and viscosity loss. Residual chlorine sensors located downstream of the mixers are used to control the rate of chlorine addition. From this sampling point, the pulp continues to an upflow tower and then to the chlorination washer.

CHEMISTRY

The Chlorine-Water Equilibrium

Chlorine dissolved in water may be present in several forms, depending on pH. Effects of pH changes on the chlorination process arise, in part, from interconversion between two of these forms, according to the following chemical equilibrium:



Addition of acid or chloride ion forces this equilibrium from right to left. As a result, at very low pH, below 1, nearly all of the chlorine is present as molecular chlorine. If the pH is increased, it is progressively converted to hypochlorous acid, conversion being complete at a pH of about 5. This is significant because hypochlorous acid reacts less rapidly with lignin than chlorine and has a greater tendency to attack carbohydrates. Dilution of brownstock with chlorination stage filtrate is one way of keeping the chlorination pH low.

Lignin Reactions

Chlorine reacts with lignin to cause part of it to dissolve immediately and a larger part to become soluble in the subsequent caustic extraction stage. Immediate solubilization is a result of oxidation reactions that fragment the lignin molecule, destroy aromatic rings and introduce hydrophilic carboxylic acid groups. Solubility in the caustic extraction stage is conferred by substitution of chlorine into the aromatic ring as well as by oxidation; alkaline hydrolysis in the extraction stage converts the chlorine substituents to solubilizing phenolic hydroxyl groups. Roughly half of the chlorine is consumed by oxidation reactions, which are generally more productive than substitution reactions.

Both molecular chlorine, Cl_2 , and hypochlorous acid, HOCl , are capable of oxidizing lignin, while only molecular chlorine is capable of substitution reactions. Chlorine reacts with lignin much more rapidly than hypochlorous acid does, so decreasing the pH enhances the chlorination rate. It also enhances the rate of lignin solubilization and removal.

Carbohydrate Reactions

Chlorine reacts with cellulose and hemicellulose, but at a much lower rate than with lignin and by a different kind of reaction mechanism. Carbohydrate

degradation during chlorination is avoided by exploiting these differences.

One undesirable reaction is cellulose chain breakage through free radical attack by chlorine. Another occurs when chlorine or hypochlorous acid oxidizes cellulose, thereby introducing carbonyl groups into some of its monomeric units. These units thereby become "weak links"; the chain is subsequently broken at these points by alkali in the extraction stage.

Lignin acts as a free radical scavenger and so, as long as there is an appreciable amount of residual lignin, the cellulose will not be damaged much. Chlorine dioxide also acts as a free radical scavenger and also protects the cellulose.

RATE AND EXTENT OF REACTION

In well mixed suspensions of kraft pulp, chlorine consumption and lignin solubilization are both extremely fast. Figure 2, for example, shows that in the presence of excess chlorine two-thirds of the lignin in a kraft pulp was solubilized within 4 seconds, and 85% in 30 seconds. At longer times, however, not very much additional lignin was solubilized. These observations may be summarized by saying that an initial rapid reaction quickly undergoes a sharp reduction in rate and then slowly approaches an asymptotic limit. The limit corresponds to a part of the lignin that cannot be removed in a single chlorination and caustic extraction.

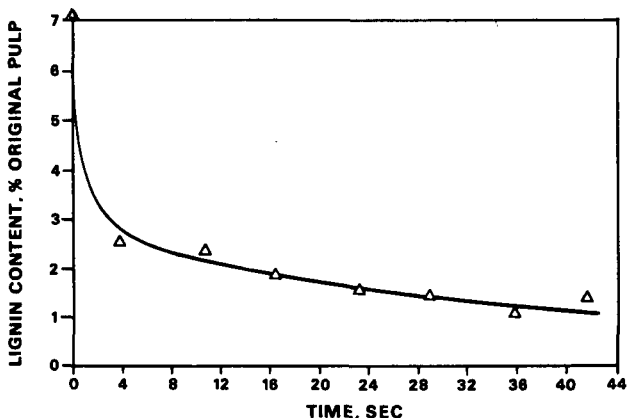


Figure 2. Early stages of kraft pulp chlorination (2).

The sharp rate decrease and limiting lignin content are features of the chlorination reaction that govern many aspects of chlorination stage operation. They also make the task of modeling the process a difficult one and serve to demonstrate its complexity on the microscopic and molecular levels. One recently proposed hypothesis (3) accounts for them on the basis of physical blockage of pores within the fiber wall by chlorinated lignin. Another (4) postulates the formation of "blocking groups" that chemically retard the chlorination of the last part of the residual lignin. Both are consistent with the observation that another chlorination following caustic extrac-

tion will rapidly reduce the lignin content to a lower limiting value (Fig. 3).

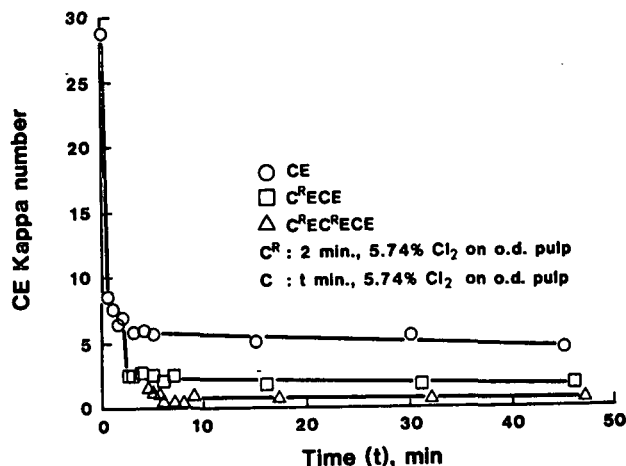


Figure 3. Effects of repeated chlorination and extraction on lignin removal (4).

PROCESS VARIABLES

Chlorine Charge

The chlorine charge, the amount applied to the pulp, is less relevant than the amount that is actually consumed (applied minus residual). Pulp viscosity loss, for example, depends mainly on the amount consumed. It is therefore important, in assessing the effect of changes in chlorine charge, to take into account the levels of the other process variables. These include unbleached pulp lignin content (K no. or kappa no.), temperature, consistency and stock flow; all influence the degree to which the applied chlorine is consumed by the pulp. One way to do this is to establish, for a particular system, the relationship between applied and residual chlorine at fixed levels of the other variables. Another is to adjust conditions to give zero residual.

As the chlorine charge (and consumption) is increased, the amount of lignin remaining after caustic extraction will, of course, decrease, but each incremental increase in charge has less effect than the previous one. This is apparent in Fig. 4, which also shows that the amount of chlorine required for any given degree of delignification decreases as the lignin content of the incoming pulp (as measured by K no.) is decreased. One method of dealing with this is to ratio the chlorine charge to the lignin content to maintain a fixed "chlorine multiple" or "kappa factor". Thus, in a specific bleach plant, one might adopt the rule that the chlorine charge should be targeted to be equal to the kappa no. of the incoming pulp multiplied by, say, 0.22 (or to the K no. multiplied by 0.33). Using this rule will not result in the same CE K no. for different unbleached K no.'s, as can be seen from Fig. 4. Each pulp has a limiting or "floor level" lignin content that is lower for pulps of lower unbleached K no., so targeting for a constant CE K no. would result in excessive chlorine use during periods of unusually high incoming K no.

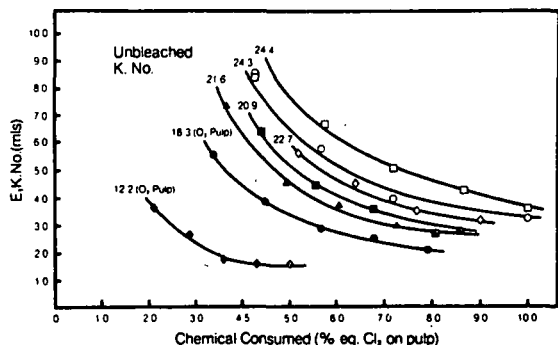


Figure 4. Effect of chlorine consumption (with 10% ClO₂ substitution) on K number after extraction (5).

The appropriate amount of chlorine to apply will not only vary with the lignin content (K no. or kappa no.) of the incoming pulp, but will also be different for different bleaching sequences, as shown in Fig. 5. In general, longer sequences having more stages over which to spread the work, demand that less be done in the chlorination stage and do not benefit from high chlorine applications. Note, however, that the use of oxygen in the extraction stage may significantly decrease the optimum chlorine charge.

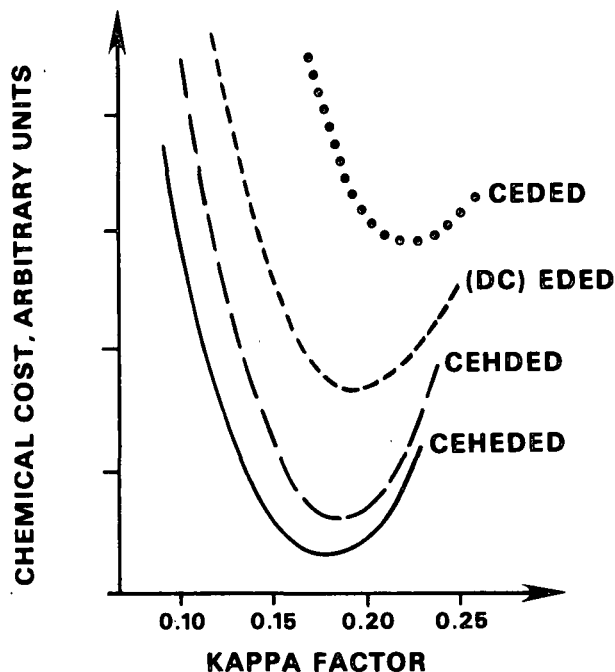


Figure 5. Optimum chlorine applications for various sequences (6).

Another important factor to consider when choosing the amount of chlorine to be applied is its effect on cellulose degradation, as indicated by pulp viscosity measured after the extraction stage. As chlorine consumption is increased, pulp viscosity continuously decreases. This is illustrated by the data in Fig. 6, which were obtained by chlorination to zero residual in the presence of a small amount

of chlorine dioxide as viscosity protector.

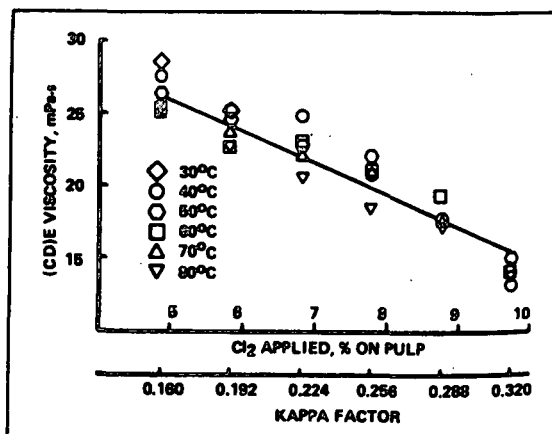


Figure 6. Effect of chlorine charge on viscosity after extraction (7).

The chlorination stage viscosity loss that can be tolerated will depend on the bleaching sequence. Curves analogous to those in Fig. 5, but with viscosity instead of chemical cost as criterion, can be experimentally constructed for a given sequence. The kappa factor that gives the best fully bleached viscosity is often close to the one that minimizes chemical cost (6,7).

Chlorine Dioxide Substitution

Adding chlorine dioxide to the chlorination stage protects the cellulose fraction of the pulp from being extensively damaged by chlorine. Cellulose degradation occurs primarily by free radical reactions, which are inhibited when chlorine dioxide, itself a stable free radical, intercepts harmful intermediate radicals.

Because the main function of chlorine is to oxidize lignin, and chlorine dioxide is an effective oxidizing agent, the chlorine dioxide added can displace part of the chlorine charge. It turns out that for effective viscosity protection, only a small amount of chlorine (5-15%) needs to be substituted by chlorine dioxide. As discussed in detail in a later paper, larger amounts can be used to obtain other benefits when circumstances warrant it.

When viscosity protection is the motivation for chlorine dioxide addition, the small amounts necessary must be added either with the chlorine or slightly later than the chlorine. This is illustrated by Fig. 7, which also shows that larger amounts of chlorine dioxide give no further improvement in viscosity. If the chlorine dioxide is added too soon, it will be rapidly consumed by the unchlorinated pulp lignin, and none will remain to protect the cellulose during the remainder of the chlorination period.

Temperature

Historically, chlorination stages were run on stock that was diluted with fresh, cold water. Since then, restrictions on fresh water usage have

forced the use of recycled chlorination filtrate or other process streams for stock dilution, and chlorination temperatures have risen.

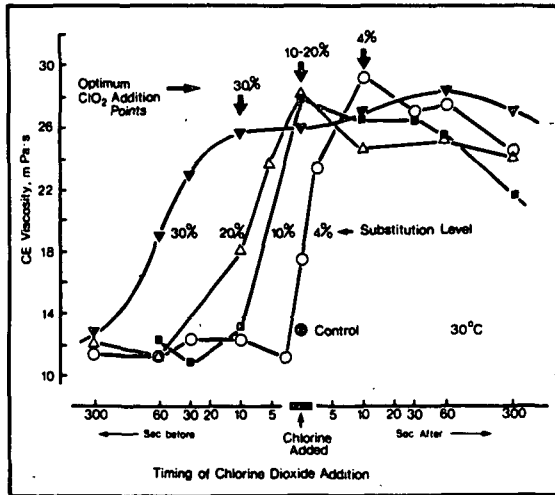


Figure 7. Effects of timing of ClO_2 addition and substitution level on viscosity after extraction (8).

Increasing the temperature accelerates both the delignification and the carbohydrate degradation reactions, increasing the danger of serious viscosity loss. With good control and the use of a small amount of chlorine dioxide, however, this danger is averted.

Increasing the temperature sharply increases the overall rate of chlorine consumption, as shown in Fig. 8. With good control and the use of a small amount of chlorine dioxide, however, cellulose is not degraded to any greater extent than at low temperature, as shown in Fig. 6. Similarly, Fig. 9 shows that the degree of delignification is unaffected.

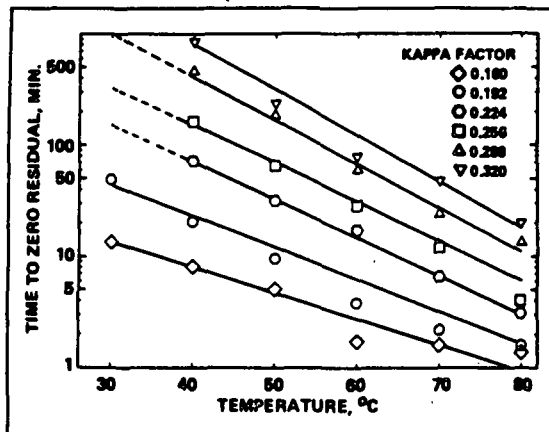


Figure 8. Effect of temperature on time to zero residual (7).

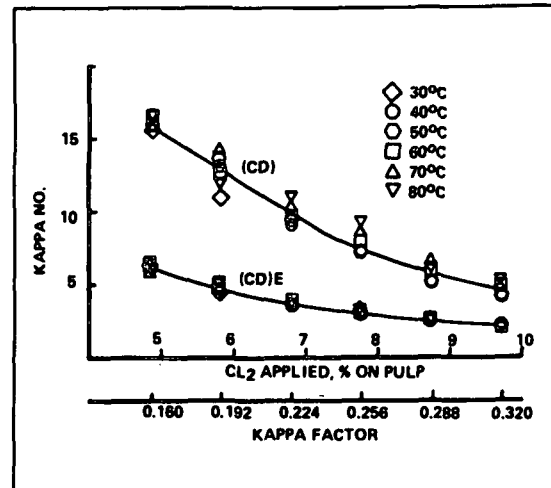


Figure 9. Effect of temperature on extent of delignification (7).

Time

The rapid initial phase of chlorination is complete in less than 2 minutes at 30 degrees C. It consumes about 75% of the chlorine and results in removal of 90% of the lignin that is removed in a 45 minute chlorination (8). Nevertheless, it is necessary to allow time for completion of the subsequent slow phase for economical attainment of high final brightness. Even at higher temperatures, where both phases are complete and all the chlorine is consumed in 5-10 min, having a 30 to 40 minute retention tower will allow complete chlorination over a wide range of upset conditions.

pH

As mentioned earlier, chlorine in water exists in equilibrium with hydrochloric and hypochlorous acids and consequently has a low pH. Furthermore, its reactions with lignin generate additional hydrochloric acid as a byproduct, so chlorination pH is typically about 2 in the absence of disturbing factors. Black liquor carryover tends to increase it, and dilution of brown stock with acidic recycled chlorination filtrate decreases it.

Decreasing the pH retards carbohydrate degradation, probably by suppressing the formation of hypochlorous acid (Fig. 10), and slightly favors delignification. Recycling chlorination filtrate to decrease the pH is therefore advantageous.

Black liquor carryover is normally neutralized rapidly in the initial stage of chlorination or upon dilution of brown stock with recycled filtrate. Under certain conditions, carryover may result in unacceptably high pH if the pulp is not preacidified. This can occur in mills with inadequate washing or in hardwood lines where the amount of chlorine required is too small to achieve a low pH; this is especially likely when chlorination follows oxygen delignification.

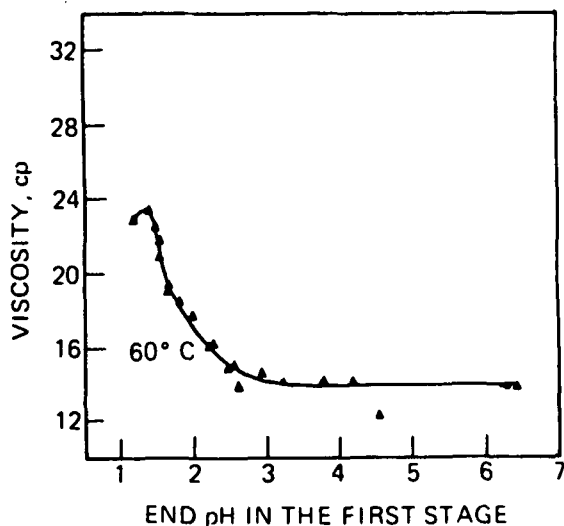


Figure 10. Effect of chlorination pH on viscosity after extraction (9).

Consistency

The advent of medium consistency mixing and pumping technology has made it possible to conduct chlorination stages at 10% consistency by injecting gaseous chlorine directly into the pulp suspension. Laboratory studies (10,11) have indicated that doing so slightly improves delignification efficiency and selectivity. A report from a recent commercial installation (12) suggests that multiple injection points, each with its own mixer, are desirable.

CHLORINATION SYSTEMS

Process Components

Analysis of the flowsheet in Fig. 1 yields the following list of operations:

- brown stock dilution
- blending and consistency control
- chemical injection and dispersion
- mixing
- control of chemical addition
- retention
- washing

Some of these are generic process components that the chlorination stage has in common with other bleaching stages, but several of them merit discussion with specific reference to chlorination.

Stock Dilution

Brown stock is diluted at the base of the high density storage tower and pumped to a blend tank. The dilution liquid can be recycled chlorination filtrate, fresh water, or some other process stream. Each has its own operational implications. Using

recycled chlorination filtrate, for example, depresses the pH and raises the temperature of the chlorination stage. Since both of these changes have beneficial effects, filtrate recycle is widely practiced.

The advantages include (5):

- low or nonexistent residual chlorine levels in the washer vat, reducing corrosion, chlorine escape, and chlorine usage,
- improved control through decreased temperature variation and faster sensor response,
- lower water usage and effluent volume, and
- smaller steam requirement in the extraction stage.

The principal disadvantage of chlorination filtrate recycle is in retrofitting in older mills where it may require upgrading brown stock piping, chlorine mixing and control strategy and hardware. The washer may not require upgrading, since in many instances the diminished vat residual decreases the corrosion rate more than the increases in chloride and acid concentration and temperature will increase it, i.e., the corrosion rate is lower with higher temperature operation.

Recently, concern has been expressed about the possible effects of filtrate recycle on the generation of undesirable chlorinated organic compounds, notably dioxins and furans (13). On the other hand, independent studies have indicated that the elimination of these compounds from chlorination effluents may be achievable by means other than discontinuing filtrate recycle (14).

Blending and Consistency Control

Stock at 3 to 4% consistency is pumped from high density storage to an agitated blend tank, which serves to smooth out fluctuations in K no. and consistency. Minimizing short term variations in both of these variables is important to facilitate control of chlorine addition. Dilution should be controlled at two points, out of the storage tower and out of the blend tank, to minimize consistency variations.

Chemical Injection and Dispersion

Chlorine is not very soluble in water, so it is not practical to predissolve it. To distribute it uniformly throughout the stock suspension and to enhance its rate of dissolution, it must first be dispersed in water as small bubbles. Dispersers are normally of the venturi type, although in-line static mixers are also used. The disperser must be small enough to produce the required pressure drop and turbulence, and there must be sufficient water to maintain a stable dispersed gas phase.

Dispersers are best operated with a cold water supply, but hot water or filtrate can be used if appropriate precautions are taken. Reeve and co-workers, in a laboratory study (15), found that cold water dispersed chlorine into bubbles averaging less than 1 mm in diameter. With hot

water, the same bubble size could be created in the initial dispersion but significant coalescence occurred within a quarter of a second. The practical significance of these results is that the dispersion must be added to the pulp immediately, before coalescence can occur, and that the mixer should be as close as possible to the injection point.

It is also important to ensure an adequate flow of water to the disperser. In the laboratory, at least 60 kg of water per kg of chlorine was required to form stable dispersions and prevent slug flow. In industry, some dispersers using as little as 40 kg of water per kg of chlorine are found.

Chlorine dioxide, when added at low levels for viscosity protection, may be mixed with the chlorine or injected into the stock line downstream of the point at which the chlorine dispersion is injected. Some installations add the chlorine dioxide between two static mixers, with the chlorine being injected just before the first one.

Mixing

Good mixing is necessary to distribute the chlorine evenly throughout the pulp and thereby to minimize the distance over which the chlorine must be transported by diffusion, which is very slow. Poor mixing impedes good sensor performance and leads to local overchlorination. It can result in dirty pulp, loss of strength and persistent residual, with its attendant problems.

Chlorine mixers are predominantly of the static, in-line type. They have mixing elements built into the stock line that function by repeatedly subdividing the flow and by inducing turbulence and radial mixing. These mixers must be carefully sized so that the velocity through them is great enough to ensure good mixing but not so great as to produce prohibitively high pressure drops.

Recently, high shear mechanical mixers have been introduced which mix chlorine gas, without prior dispersion, directly with the pulp suspension. Some results show improved performance over static mixers.

Prior to the successful introduction of in-line static mixers, chlorination mixers were small stirred tanks providing mild agitation and blending. The retention time was commonly twenty seconds to a minute with some earlier types providing several minutes retention and several agitators. These mixers are more expensive to buy and operate than static mixers, and less effective.

Control of Chemical Addition

The objective of chlorination control should be to maintain the desired relationship between chlorine consumed (not applied or residual) and incoming pulp lignin content. This is achieved by feedback control of the level of chemical addition in response to measurements of degree of chlorination or residual chlorine concentration at one or more points downstream of the point of chlorine addi-

tion. These measurements may be made just after chlorine addition, after the retention tower, in the washer vat, or after the extraction stage. In general, the time delay should be short enough to allow effective control action and long enough to provide a meaningful basis for that action. Measurements may be made manually (vat residual titration, CE K no.) or, preferably, by sensors.

Optical sensors are used to determine degree of chlorination. They are based on absorbance of light by lignin; the more it is chlorinated the less it absorbs. The sensor light source illuminates the stock flowing past the sensor, and the reflected light is measured at a specific wavelength. A similar measurement at another wavelength where lignin does not absorb is also measured to provide a baseline.

Sensors for measurement of residual chemical are of two types, ORP (oxidation-reduction potential) and polarographic. ORP sensors measure the potential difference between platinum and reference electrodes. A disadvantage of this type is that the signal is highly nonlinear, rising sharply near zero and leveling off as the residual is increased. In the polarographic sensor, the voltage appropriate for chlorine reduction is applied to a measuring electrode. The resulting current is directly proportional to the concentration of chlorine present.

Good control of the rate of chlorine addition requires a stable operating environment, which implies the need for effective control of other process variables. Primary among these are consistency, volumetric flow rate, and temperature. A stable tonnage rate depends on control of consistency and flow rate and is vital for control of chlorine application per ton of pulp. Volumetric flow rate determines the residence time between chemical addition and on-line sensor, an essential factor in sensor performance. Temperature affects chlorination rate and sensor response and must be compensated for when changes occur.

PROCESS FLOWSHEET EXAMPLES

An example of an actual operating chlorination stage flowsheet is given in Fig. 11 (16). Consistency is controlled with a temperature-controlled blend of water and recycled water. Chlorine addition is controlled by an ORP sensor, mounted in a sample line to provide the needed retention time. Chlorine dioxide, at low substitution, is added just after the chlorine for optimal strength protection.

A second example is shown in Fig. 12. In this mill, recycled chlorination filtrate is added at three places to get uniform consistency. Chlorine dioxide, at high substitution, is added in advance of the chlorine for optimal delignification efficiency, and a small amount is added with the chlorine for strength protection. The sodium hypochlorite added is a small amount of byproduct solution that is disposed of in the chlorination stage. Chlorine addition is controlled by an optical sensor.

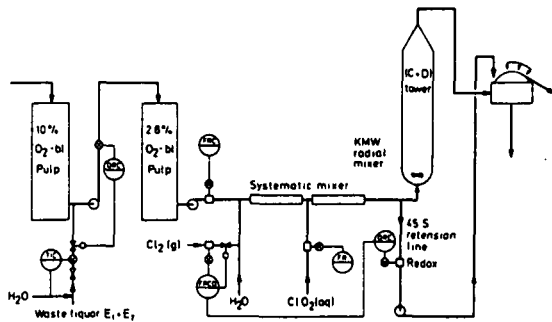


Figure 11. Chlorination Process A.

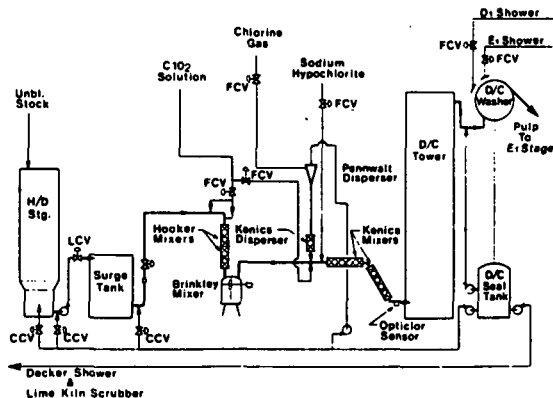


Figure 12. Chlorination Process B.

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