Optimal use of hydrogen peroxide

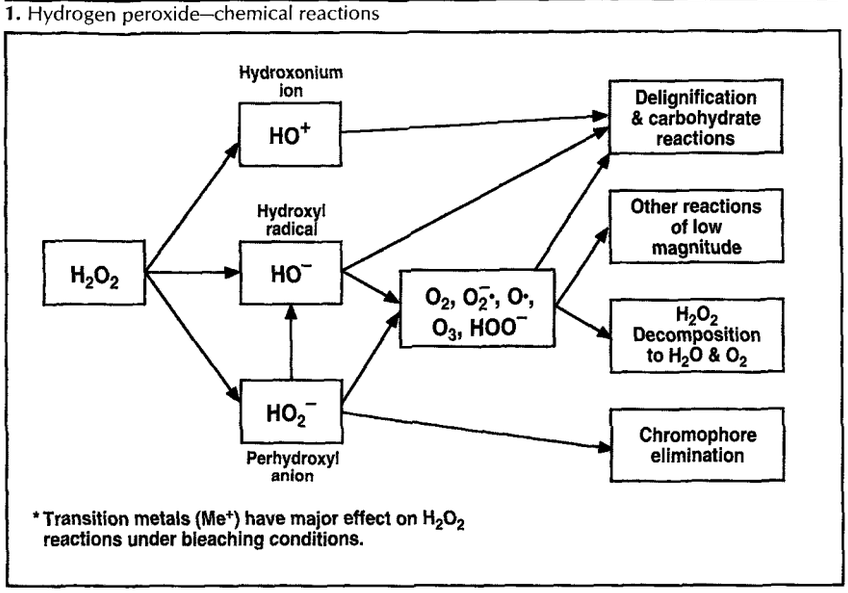
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The process of kraft pulp bleaching has undergone considerable changes in recent years. These changes are primarily an effort on the part of the mill to improve the quality of the final bleached pulp, reduce the impact on the environment, and improve the economics of the process.

Hydrogen peroxide use in the bleaching process to reduce or eliminate chemicals such as sodium hypochlorite and chlorine gas is one method to achieve these changes. Its use in the bleach plant has been proven on the mill scale, and its optimal use is a key to the modern elemental chlorine free (ECF) bleaching process.

The optimal use of hydrogen peroxide in the alkaline extraction stages requires careful observation and control of various operating parameters involved in the bleach plant. Under optimal conditions, hydrogen peroxide can provide numerous beneficial results. These include increased final brightness or reduced requirement for other bleaching chemicals, reduction in brightness reversion of bleached pulp in the downstream papermaking process, reduced level of chlorinated compounds in mill effluent, reduced color of mill effluent, and reduced bleaching chemical costs.

1. Hydrogen peroxide—chemical reactions



General chemistry of H_2O_2 in pulp bleaching

The way in which hydrogen peroxide reacts must be controlled in order to ensure that its maximum potential is realized in the bleach plant. When applied to kraft pulp in the bleaching process, hydrogen peroxide will generally react via three intermediate species. Which of these species is formed is dependent on the pH of the stock and the presence of certain metals in the pulp when hydrogen peroxide is added. These three species are typically associated with the following conditions:

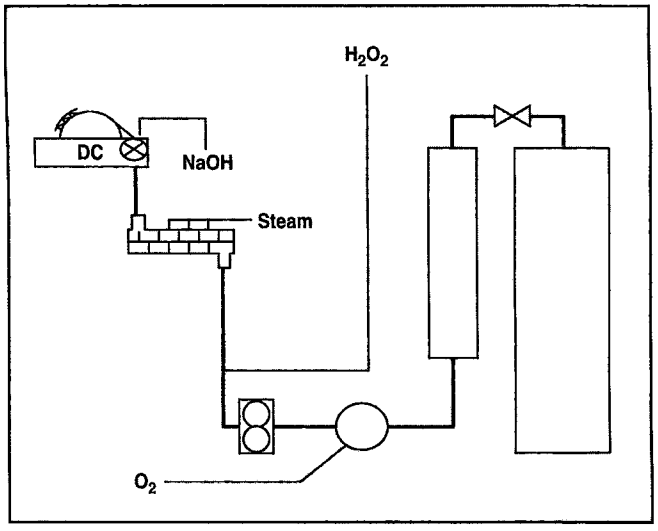
1. Hydroxonium ion (HO^+) under acidic conditions;
2. Perhydroxyl anion (HOO^-) under alkaline conditions;
3. Hydroxyl radical ($HO\cdot$) in the presence of transition metals such as manganese and iron.

The ways in which hydrogen peroxide reacts with pulp are shown in **Fig. 1**. This figure shows the original hydrogen peroxide on the left side and the conditions under which each of the intermediate species form. On the far right are the final reactions hydrogen peroxide undergoes with either the pulp or toward decomposition. The desired final results in this figure for pulp bleaching are delignification and chromophore elimination (brightening). These two results are favored by reaction of the hydrogen peroxide under alkaline conditions with little or no transition metals (Me^+) present. The carbohydrate reactions of hydrogen peroxide will result in pulp strength loss. Other reactions such as decomposition can result in waste of hydrogen peroxide.

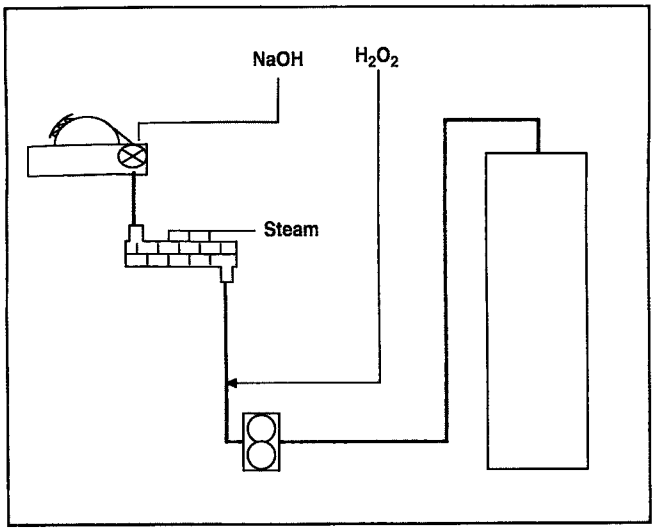
H_2O_2 and alkaline extraction

The application of hydrogen peroxide in the first alkaline extraction stage (E1 stage) is effective for delignification and pulp brightening. Pulp at this stage will still contain a considerable amount of lignin, so a focus on delignification here is of

2. EPO stage



3. E2 stage



greatest benefit. Steps along the delignification reaction pathway include prior pulp treatment, the addition sequence of chemicals and equipment layout in the E1 stage, concentration of hydrogen peroxide at application, and proper control of conditions in the stage.

The typical E1 stage immediately follows a chlorination stage that uses a mixture of chlorine and chorine dioxide or all chlorine dioxide. The low pH of the chlorination stage can have an effect on the hydrogen peroxide used in the E1 stage because of the removal of metal ions from the pulp as pH is decreased. At the very low pH of a conventional low-substitution chlorination stage, most of the metal ions in the pulp are dissolved and separated from the pulp on the chlorination stage washer. With low pH, the possibility of transition metals affecting the hydrogen peroxide reaction pathway is minimal. As the pH of the chlorination stage rises with increased substitution of chlorine with chlorine dioxide, fewer metal ions may be removed from the pulp. If this reduction is significant, the reaction pathway of the hydrogen peroxide may be altered and become less efficient. In this case, it may be necessary to reduce the pH of the chlorination stage or apply a chelating agent to the pulp prior to the E1 stage to effectively remove transition metals. Most chelating agents have to be washed out of the pulp before reaching the high alkaline or low acidic range.

In addition, contamination of the pulp with organic material or other chemicals can result in waste of hydrogen peroxide. It is fairly common practice to use a portion of the E1 stage filtrate on the last showers of the chlorination stage washer. This practice may decrease the caustic requirement as well as conserve energy required to heat the stock in the E1 stage. This filtrate can, however, contain a relatively large amount of organic material. If the stock entering the E1 stage contains a high amount of organic material, the filtrate may consume much of the hydrogen peroxide, robbing the pulp of the full bleaching potential.

The presence of other active bleaching chemicals such as residual chlorine or chlorine dioxide will also consume hydrogen peroxide. In this reaction, the active chlorine residual is reduced and water and oxygen from hydrogen peroxide are produced. Because of these possible reactions with hydrogen peroxide, it may be necessary to limit the amount of E1 stage filtrate or use a fresh water stream for the last showers on the chlorination stage washer.

The chemical addition sequence when hydrogen peroxide is used in the E1 stage influences the desired final result. As shown in Fig. 1, the desired reaction pathway begins under alkaline conditions; so, it is most desirable to apply the caustic to the pulp prior to hydrogen peroxide injection. If hydrogen peroxide contacts pockets of extreme alkalinity or high pH, some decomposition may occur. This possibility can be reduced by ensuring that the application points of caustic and hydrogen peroxide are as far apart as possible with good mixing of both chemicals.

Figure 2 shows a typical equipment layout for applying both hydrogen peroxide and oxygen in the E1 stage. In this scheme, caustic is mixed at the washer repulper and steam mixer, and peroxide is mixed at the stock pump and oxygen mixer.

The optimum effect occurs when hydrogen peroxide is applied at a concentration of 5–10 wt%, requiring dilution of the typical 50 wt% solution. Use a clean water stream for dilution to ensure no decomposition of hydrogen peroxide from metals or other organic materials, as discussed previously. Dilution of hydrogen peroxide allows for easier control of the application rate. Typical flow rates of 50% hydrogen peroxide are <1 gal/min while greater flow rates, normally associated with dilute solution, are more easily controlled. Dilution also allows for improved mixing of hydrogen peroxide with stock and can slightly slow the reaction rate, resulting in a more uniform effect.

Under typical conditions in the E1 stage—relatively high lignin content, moderate alkalinity, high temperature, and

medium consistency—hydrogen peroxide reacts relatively quickly. In general, with typical hydrogen peroxide charges in the range of 3–9 lb/ton, approximately 90% of the original hydrogen peroxide charge is consumed within 10 minutes after application. At this point, the residual peroxide can be difficult to measure accurately due to the inability to obtain a sample and also due to the test method. In practice, absence of a hydrogen peroxide residual at the end of the stage is common. If the hydrogen peroxide doesn't seem to be working, check for hydrogen peroxide residual closer to the application point for insights into the possibility of decomposition or other undesirable reactions.

As shown previously, proper pH control is critical for optimal hydrogen peroxide use. Proper control will allow for an adequate caustic charge to maintain a pH at the end of the reaction in the 10.5–11.0 range. To improve control, a pH instrument is typically installed somewhere shortly after the chemical addition point to control the caustic flow rate. The addition of hydrogen peroxide, which is acidic, will tend to cause a slight decrease in the stock pH through the E1 tower. A typical pH decrease of 0.3 to 1.0 unit is observed and requires that a pH instrument at the entrance to the E1 tower be controlled generally in the 10.8–11.5 range.

H_2O_2 in the E2 stage

Hydrogen peroxide application in the second alkaline extraction stage (E2 stage) is also effective for delignification and brightening of the pulp. Here, however, the pulp typically has a relatively low lignin content and a focus on brightening will yield the greatest benefit. Therefore, the pathways shown in Fig. 1 which result in chromophore elimination (or brightening) are desired. As in hydrogen peroxide application at the E1 stage, practical aspects in the bleach plant to ensure this reaction pathway include prior pulp treatment, the addition sequence of chemicals and equipment layout in the E2 stage, concentration of hydrogen peroxide at application, and proper control of conditions in the stage.

In general, conditions for hydrogen peroxide application in the E2 stage should match those of the E1 stage. Contamination of the stock entering the E2 stage with metals, organic materials, or active chlorine will reduce the efficiency of washing from the previous bleaching stage.

The chemical addition sequence and equipment layout for hydrogen peroxide application in the E2 stage, shown in **Fig. 3**, is similar to that in the E1 stage. Again, caustic is added, with good mixing, at a point as far away as possible from the hydrogen peroxide application point. The mixing efficiency available in this stage is typically not as good as in the E1 stage but should be sufficient for proper results.

The reaction rate of hydrogen peroxide in the E2 stage is somewhat slower than in the E1 stage because there are fewer pulp reaction sites available. Trace or less residual hydrogen peroxide should be measured at the end of the retention tower. With the reduction of available reaction sites in the E2 stage, a slightly milder pH is desired. Typically, an end pH in the 10.0–10.5 range is sufficient to provide desired results.

Summary

Efficient use of hydrogen peroxide in the modern kraft pulp bleaching sequence is important to ensure adequate pulp quality, minimal environmental impact, and acceptable bleaching chemical costs. Its optimal use can be ensured by controlling the pathways in which hydrogen peroxide reacts to achieve the desired results of pulp delignification and brightening. Critical parameters in controlling the hydrogen peroxide reactions include absence of metals and other inhibiting material, sequence of chemical addition and equipment layout in the stage, concentration of hydrogen peroxide at application, and good control of the stage. ■

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