

Hydrogen peroxide: innovations in chemical pulp bleaching

Patricia B. Walsh

Hydrogen peroxide can function as a replacement for hypochlorite in chemical pulp bleaching.

As analytical methods for mill effluents change, environmental legislation seems to follow suit, and for pulp mills the issue has been a real chameleon. From BOD to mercury levels to dioxin to TOCl, regulations change again and again. Now, just as mills bring their operations under "safe" chlorination levels, they face new regulations on the discharge of adsorbable organic halogens (AOX). Legislation already in effect in some areas sets maximum AOX limits at ≤ 1.5 kg/metric ton, which is below that of some mills currently operating within the dioxin "safe zone."

Increasingly stringent regulations, such as those mentioned above, are a major driving force behind innovation in the pulp and paper industry. Clearly, the way to reduce dioxin, furan, chloroform emissions, and AOX discharge is to reduce the chlorinated compounds used in the bleaching process. But because of variations from mill to mill, no universal answer exists. Differences in pulping method, wood species, equipment, and desired pulp quality determine the kinds of chemistry and process changes required.

As we rethink pulp bleaching, we see that hydrogen peroxide plays an evolving role in the future of the pulp and paper industry. Traditionally, the use of hydrogen peroxide was limited to the second caustic extraction stage or high-density storage, in order to reduce chlorine dioxide consumption or to provide 1-2 points of additional brightness.

But today, in chemical pulp bleaching, hydrogen peroxide finds a growing spectrum of applications. It functions as a replacement for hypochlorite, either partially or totally. It can be used in the first extraction stage with or without oxygen to help reduce oxidant levels in the chlorination stage. Hydrogen peroxide continues to reduce demands for chlorine dioxide; and it continues to find use in the high-density storage chest, where it effectively adds an extra bleaching stage.

When used in the bleaching of chemical pulps, hydrogen peroxide produces a less-colored effluent, reduces pollution load on the effluent treatment system, and improves

product quality—as is apparent in strength, brightness, and brightness stability.

Other advantages of hydrogen peroxide include environmental compatibility and stability in commercial storage. Its reaction by-products are just water and oxygen, and when properly stored its decomposition rate is less than 1% per year.

H₂O₂: replacing hypo

Hydrogen peroxide, easily added to an existing bleach sequence without process interruption, can replace hypochlorite either partially or completely.

Because hypochlorite tends to attack both lignin and cellulose, pulp quality can be improved when hydrogen peroxide is used as a replacement. This increases pulp viscosity and reduces brightness reversion. It also gets rid of a major source of chloroform and allows for leveling of the bleach plant temperature profile—thereby reducing steam costs and improving bleaching efficiency.

Hydrogen peroxide can effectively replace hypochlorite in the bleaching of kraft pulps in CEHDED sequences, CE/HDED for both hardwoods and softwoods, in CEHED and CEHD sequences for hardwoods, and in the bleaching of sulfite pulps. Hydrogen peroxide can also replace or reduce hypochlorite requirements in CEHED and CEHD sequences for softwoods.

Case study 1

As an example, a Southern hardwood kraft mill experienced problems following conversion to an R8 chlorine dioxide generator, which eliminated the scrubber hypo used in the caustic extraction stage and adversely affected final brightness and chlorine dioxide usage. To solve this problem, the mill replaced hypochlorite with hydrogen peroxide. **Table I** shows the results.

In this case, hydrogen peroxide replaced hypochlorite at a ratio of 1:3.5. The CEK was reduced 23%, and the chlorine dioxide charge in the D stage was reduced by 7.2 lb/ton. The final brightness increased 1.4 points, while final pulp properties (viscosity and dirt) remained at pretrial levels.

Walsh is development manager, Interlox America, P. O. Box 27328, Houston, Tex. 77098.

I. Southern hardwood kraft

	<i>C/DE/HD → C/DE/PD</i>	
NaOCl, %	1.5	0
H ₂ O ₂ , %	0	0.43
CEK	3.1	2.4
ClO ₂ (D stage), %	1.3	0.94
Final brightness	87.1	88.5
Final viscosity	17.8	17.8
Final dirt count	3.0	3.1

II. Northwest blended softwood kraft

	<i>CEHD → CE/PHD</i>	
NaOCl, %	2.15	0.8
H ₂ O ₂ , %	0	1.0
ClO ₂ (D stage), %	0.43	0.27
Brightness	80.7	82.0
Final effluent:		
AOX kg/a.d. metric ton	5.1	3.7
CHCl ₃ , kg/a.d. metric ton	0.352	0.178

III. Southern pine kraft

	<i>C/DEHD → C/DE/PHD</i>	
NaOCl, %	3.0	1.5
H ₂ O ₂ , %	0	0.75
CEK	4.1	3.0
ClO ₂ (D stage), %	0.35	0.40
Final brightness	87	87-88
Final viscosity	9.0	9.2

IV. Softwood kraft

	<i>C/DE/OD → C/DE/OD(P)</i>	
ClO ₂ (D stage), %	1.2	1.2
H ₂ O ₂ , %	0	0.15
Brightness:		
D stage	85-88	85-88
High density	84-86	88-90.5

Case study 2

At a Northwest mill, environmental concerns and upcoming regulatory restrictions on chloroform and AOX discharges initiated interest in using hydrogen peroxide as a partial replacement for hypochlorite. They converted an existing CEHD sequence to a CE/PHD sequence. **Table II** shows the results.

In this case, hydrogen peroxide replaced hypochlorite at a ratio of 1:1.4. Chlorine dioxide usage was reduced by 3.2 lb/ton. AOX discharge was reduced by 27.5%, and chloroform discharge was reduced by 49.4%.

Case study 3

In another case, a Southern pine kraft mill experienced excessive fiber degradation and brightness reversion due to heavy reliance on hypochlorite in the bleaching sequence. To solve this problem, hydrogen peroxide was applied at 15 lb/ton in the caustic extraction stage of a C/DEHD sequence. **Table III** shows the results.

The addition of a hydrogen peroxide reinforced extraction stage allowed for a 50% reduction in hypochlorite usage. The pulp viscosity was improved slightly, and although the bleach plant brightness was marginally higher, the final paper machine brightness increased four points due to less reversion.

H₂O₂: reducing demand for chlorine dioxide

Production capacity at many pulp mills is limited by the output of chlorine dioxide generators. Compared to the high cost of adding new generators, hydrogen peroxide substitution represents a low-capital option.

In a five-stage C/DEDED sequence, adding hydrogen peroxide to the second extraction stage can significantly

reduce requirements for chlorine dioxide in D1 and D2. Ratios of one pound of hydrogen peroxide replacing two pounds of chlorine dioxide are common. Final bleached brightness variability is also reduced.

Hydrogen peroxide, added to the first caustic stage, acts as a delignifying agent under high temperature (>170°F) and alkaline conditions, reducing CEK and thus reducing the amount of chlorine dioxide required in subsequent stages. The "excess" chlorine dioxide can be moved up front to the chlorination stage for substitution. Depending on chemical costs, delignification with hydrogen peroxide in E1 can be more economical than chlorine dioxide substitution.

By adding 0.75% hydrogen peroxide to the E1 stage of a southern pine CEDED sequence, the chlorine charge was reduced from 7.0% chlorine to 3.5% chlorine (a kappa factor of 0.11). Not only is the CE AOX reduced from 7.0 kg/a.d. metric ton to 3.5 kg/a.d. metric ton, but dioxin levels are well within the safe zone.

Hydrogen peroxide added in E1 maintained the target 5.0-6.0 CEK and allowed a 50% reduction in elemental chlorine. In mills without excess chlorine dioxide capacity, hydrogen peroxide addition to E1 is a cost-effective, easily implemented technology for meeting environmental requirements.

H₂O₂: high-density storage bleaching

The application of alkaline hydrogen peroxide to pulp in the high-density storage chest effectively adds an extra bleaching stage. Brightness stability improves substantially on both softwood and hardwood pulps, with brightness gains of 1-3 points on softwood kraft pulps. Brightness gains are less dramatic with hardwoods.

High-density storage bleaching supplements and extends available chlorine dioxide, provides a means of