On-site peracids: Tools for bleaching strategies to meet the cluster rule and considerations on selecting among them

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ABSTRACT: In contrast to some nonchlorine technology options for cluster rule compliance, peracids require low investment, are easily retrofit, and can be used to both delignify and brighten pulps. They can be used to reduce kappa numbers for production of low-AOX pulps, to eliminate use of hypochlorite, and in TCF bleaching sequences, on-site processes for peroxyacetic acid, peroxymonosulfuric acid (Caro's acid), and combinations of both (mixed peracids) are options. Important differences among them with regard to safety, peracid yield, effluent loads, and operating utility are discussed to assist mills considering peracids.

KEYWORDS: Adsorbable organic halogen, bleaching, bleaching effluents, brightening, chemical reactions, chemical treatment, chlorine free bleaching, delignification, effluents, inorganic acids, organic acids, oxygen compounds, peracetic acid, peroxy acids, peroxymonosulfuric acids, recommendation, regulations, safety, spent liquors, sulfur compounds, synthesis.

With respect to chlorine-containing emissions, the cluster rule proposes three specific cases:

- Low AOX limits that effectively (a) require low kappa numbers entering the bleach plant, (b) eliminate Cl_2 use, and (c) place a ceiling on ClO_2 use
- Elimination of hypochlorite from most mills
- Elimination of all chlorine-containing bleaching chemicals from paper-grade sulfite mills.

In addition, these severe restrictions on chlorine-based delignifiers and bleaches, coupled with market interest and prospects of further closure of the bleach plant filtrate streams, have caused some kraft mills to consider the totally-chlorine-free (TCF) option, even though the Environmental Protection Agency (EPA) proposals do not require it.

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Peracids compared to other options to address the cluster rule

The previous three cases indicate two technical needs: nonchlorine methods to delignify and nonchlorine methods to brighten pulp. Numerous technologies are in various states of development or commercialization to address both of these goals. They can be considered in that context, as shown in **Table I.**

Peracids and their salts, whether from equilibrium or distilled peracetic (Pa), equilibrium Caro's acid (Px), or mixed peracids combining Caro's and peracetic acids (Pxa) can delignify and brighten pulps in low- or nonchlorine bleaching sequences *(1–8).* The requirements for building new equipment or rearranging existing equipment to use peracids are minimal *(9–12);* this is an important consideration, because many U.S. mills are constrained by limitations on capital or on space near the pulp mill. Typical facilities for on-site manufacture of equilibrium peracids require only storage (which often already exists) for the ingredients (hydrogen peroxide and

acid), pumps for ingredients and product, a reaction mixing zone, and (optionally) provisions for cooling product. Excluding ingredient storage, on-site manufacturing facilities for equilibrium peracids can be mounted on one skid that is easily transportable, and indeed such equipment has been used at mills *(9, 10)*. Distilled peracetic acid would probably have different space requirements, because it is a more complex process than the mixing operations that characterize the equilibrium processes, and there are potential hazards that are different from equilibrium peracids.

Peracids in sequences to address cluster rule issues

The following three cases illustrate the usefulness of peracids for meeting the proposed cluster rule:

- Delignifier for low-AOX bleaching sequences
- Replacement for hypochlorite
- Delignifier and brightener in TCF sulfite sequences.

Peracid as delignifier for low-AOX bleaching strategies

The EPA has proposed a very low AOX level, and the kappa number entering the bleach plant must be quite low to achieve that level. Extended cooking and oxygen prebleaching processes are being promoted for delignification. However, both processes require substantial capital to implement, and many mills are searching for alternative low-capital technologies to delignify prior to bleaching. On-site peracids can be used for this purpose and can be implemented without significant equipment modifications to the bleach plant.

Results on several different fibers show the combination of a peracid stage followed by an Eop stage typically gives at least 50% delignification, without using chlorine-containing chemicals or requiring a large capital investment. **Figure 1** compares an oxygen delignification to PxaEop on a kappa no. 34 southern pine kraft brownstock. Both reduce the kappa number by half, and the PxaEop results in somewhat higher brightness. Conditions are in **Table II,** and chemical doses are wt. % on pulp unless otherwise noted.

Figure 1 shows even better performance on kappa no. 20 kraft eucalyptus. The Pxa stage alone gives a lower kappa number than oxygen delignification, and the combination of Pxa and Eop stages results in 60% delignification, substantially more than the O stage. Viscosities were comparable. PxaEop can be quite ef-

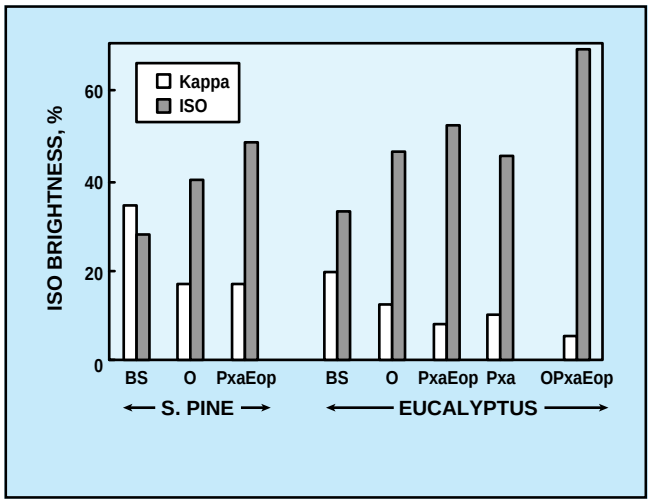
I. Methods to delignify and brighten pulp

Technology	Primary use in Delignifying	Primary use in Brightening	Investment
Extended cooking	Yes	No	High
Oxygen delig.	Yes	No	High
Ozone	Yes	Yes	High
Anthraquinone	Yes	No	Low
AQ - Polysulfide	Yes	No	Low
Peracids	Yes	Yes	Low
Peroxide			
Conventional	Yes	Yes	Low
High-pressure	No	Yes	High
High-consistency	No	Yes	High
Enzymes	Yes	No	Low

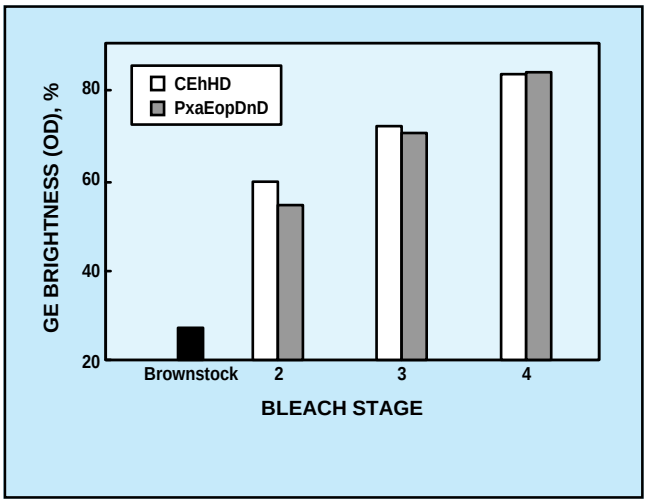
II. Peracid compared to oxygen as a delignifier

	Kappa no.	% ISO	Visc., cp
Kraft southern pine			
Brownstock (mill pulp)	34.5	28	-
PxaEop	16.8	48	-
Pxa 0.4% (AO as peracid), 70°C, 10% consistency, 60 min			
Eop 0.5% H_2O_2, 2% NaOH, 12% consistency, 85°C, 30 psig, 60 min (25 min at pressure)			
Oxygen delignification	17.0	40	-
95°C, 12% consistency, 60 min, 2.5% NaOH, 100 psig			
Kraft eucalyptus			
Brownstock (mill pulp)	19.6	32.7	44.3
Pxa	10.0	44.9	42.4
PxaEop	8.0	56.6	30.9
Pxa stages: 0.4% (AO as peracid), 80°C, 3.5% consistency, 60 min			
Eop 0.5% H_2O_2, 2% NaOH, 11% consistency, 80°C, 24 psig, 60 min (20 min at pressure)			
O Pulp (mill pulp)	12.4	46.2	30.7
OPxaEop	5.1	68.7	24.8
Pxa stage: Same as above			
Eop stage: Same as above			

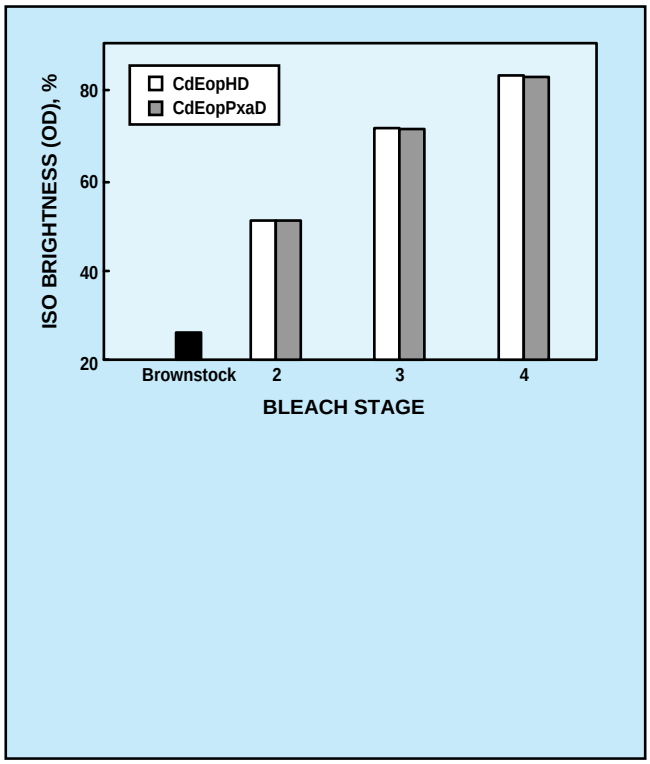
1. Peracid as delignifier—PxaEop



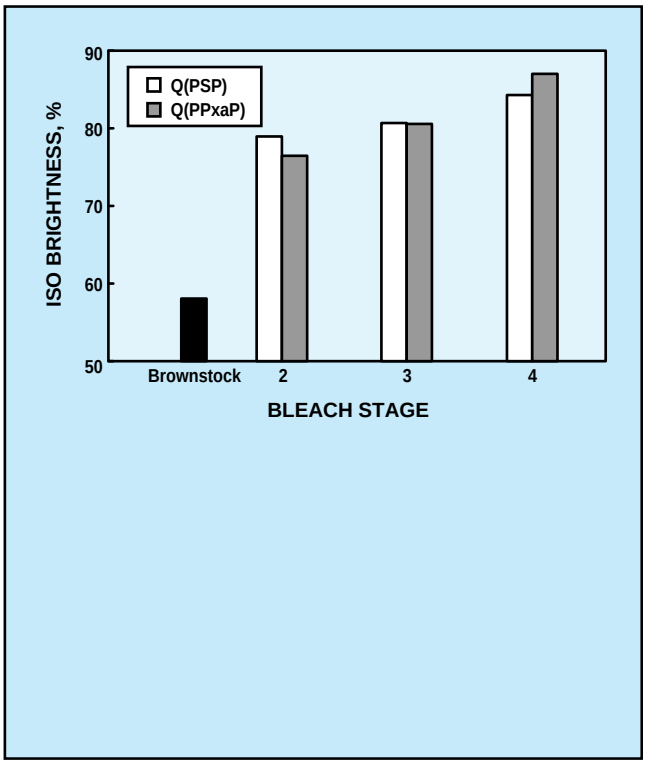
2. Peracid for low-AOX bleaching—CEhHD → PxaEopDD, U.S. mixed hardwood, kappa no. 15, GE brightness 27



3. Peracid as replacement for hypochlorite—CdEopHD → CdEopPxaD, S. pine, kappa no. 32, ISO brightness 26



4. Peracid in TCF sulfite bleaching—Q(PSP) → Q(PPxaP), softwood, kappa no. 16, ISO brightness 58



fective at further delignifying and brightening after the O stage, taking the oxygen pulp from kappa no. 12 and 46% ISO brightness to kappa no. 5 and 69% ISO.

It is useful to review the concept of expressing all peracids in terms of equivalent amounts of "active oxygen" (AO) or as an equivalent amount of a representative peracid, such as H_2SO_5 (Caro's acid). The peracids represented in this paper are referred to in these two ways. Caro's acid, with a molecular weight of 114.08 g, is represented as follows:

O
||
HOOSOH
||
O

In calculating the percent active oxygen of a peracid, only one of the

oxygens in the O-O linkage of a peracid is considered to be active. Thus, for example, H_2SO_5 is 14.0% by weight active oxygen (atomic weight of oxygen divided by molecular weight of H_2SO_5 times 100, i.e., 16.0/114.08 x 100 = 14.0%). Likewise, peracetic acid has a molecular weight of 76.05 and is 21.0% AO.

Accordingly, a weight of any peracid, or solution containing peracid, can be converted to an "equivalent H_2SO_5" weight basis by multiplying by the percent peracid active oxygen in the material and dividing by 14.0 (the percent active oxygen in H_2SO_5). For example, one pound of a material that is 5.72% active oxygen is equivalent to 5.72/14.0 = 0.406 lb of H_2SO_5.

Figure 2 shows the use of mixed peracids as a delignifier to retrofit a four-stage sequence for a northern U.S. mixed hardwood brownstock. The mill currently bleaches by a CEhHD sequence, using approximately 3.3% Cl_2 on kappa no. 15 brownstock to make mid-80s GE brightness for integrated paper operations. Details of the bleaching conditions are shown in **Table III.**

One option to reduce AOX at this mill is to install oxygen delignification and then to modify the first, second, and third stages to make an ODEoDD sequence. The bleach data (Table III and Fig. 2) show there is a peracid alternative, PxaEopDD, that does not require investment for oxygen delignification or modification of the first tower, since the peracid stage can be done at low consistency and moderate temperature. Only the second and third towers are retrofit to Eop and ClO_2, respectively, and peracids are substituted for chlorine in the first stage. The AOX should be substantially lower because the pulp kappa number, when first exposed to a chlorine-containing bleach, is less than half what it was in the CEhHD sequence (Table III). Instead of a C stage at kappa no. 15, the new sequence uses a D stage at kappa no.

III. Peracid as a delignifier for low-AOX bleaching*

	CEhHD	*PxaEopDD*
1st stage: 3.5% cons., 60 min		
Temperature, °C	50	70
Cl_2, %	3.3	-
Pxa, % AO as peracid	-	0.4
NaOH, %	-	2.6
2nd stage: 11% cons., 60 min		
Temperature, °C	50	90
NaOCl, % as available Cl_2	1	-
H_2O_2, %	-	0.5
O_2, psig, 20 min at press.	-	24
Brightness, % GE:		
Air-dried	64.7	55.5
Oven-dried	59.9	54.4
Kappa no.	2	5.9
3rd stage: 11% cons., 110 min		
Temperature, °C	55	70
NaOCl, % as available Cl_2	0.7	-
ClO_2, %	-	0.7
Brightness, % GE:		
Air-dried	77.8	72.5
Oven-dried	72.1	70.6
Kappa no.	1.4	1.7
Viscosity, cp	9	14.7
4th stage: 11% cons., 225 min		
Temperature, °C	70	70
ClO_2, %	0.45	0.45
Brightness, % GE:		
Air-dried	87.8	86.6
Oven-dried	84.0	84.5

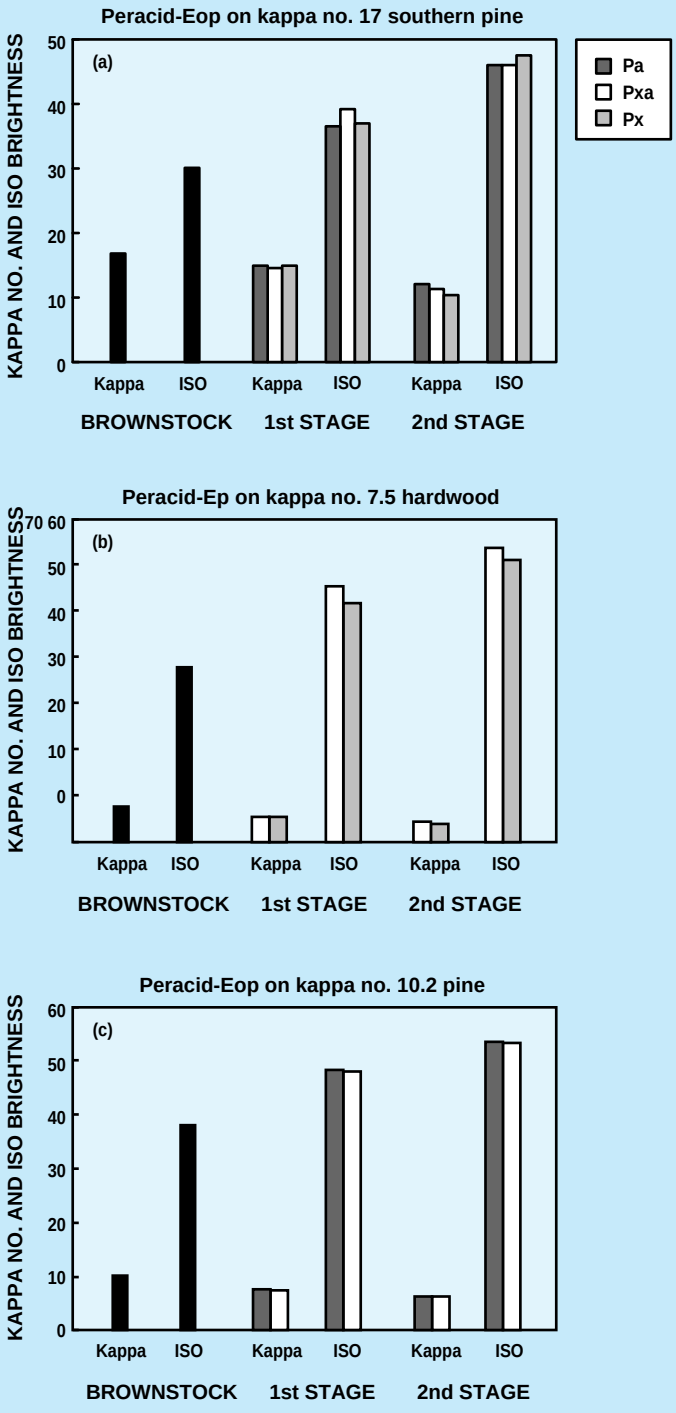
*Brownstock: Mixed U.S. hardwood kraft, kappa no. 15, 27% GE brightness, 22-cp viscosity

IV. Peracid as a replacement for hypochlorite

	CdEopHD	*CdEopPxaD*
CdEop pulp		
Brightness, % ISO	51.1	Same
Kappa no.	3.1	Same
Viscosity, cp	21.1	Same
3rd stage: 10% cons., 40 min		
Temperature, °C	45	80
NaOCl, % as available Cl_2	2	-
Pxa, % AO as peracid	-	0.2
Brightness, % ISO:		
Air-dried	78.5	75.1
Oven-dried	71.9	71.8
4th stage: 10% cons., 120 min		
Temperature, °C	70	70
ClO_2, %	0.6	0.6
Brightness, % ISO:		
Air-dried	88.0	87.4
Oven-dried	83.8	83.6
Viscosity, cp	13.7	18.5

*Brownstock: Southern pine, kappa no. 32.2, 25.7 % ISO, 28-cp viscosity

5. Delignification and brightening. Peracid + oxidative extraction sequences



5.9. In addition, the pulp viscosity is substantially improved over the CEhHD control.

Peracid as replacement for hypochlorite

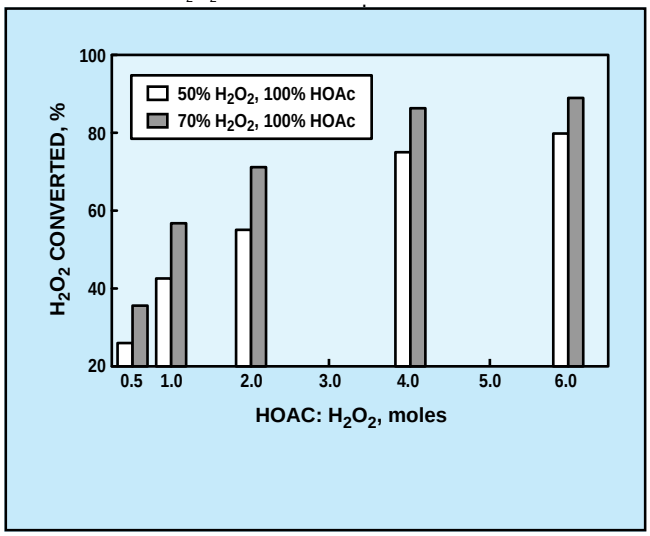
Although many U.S. mills have already substantially reduced or eliminated the use of hypochlorite, there are some cases where it is still employed. **Figure 3** and **Table IV** illustrate how a mill, using a CdEopHD sequence on southern pine, can use peracid to eliminate hypochlorite without making significant modifications to its bleach plant. Bleach residence times are unchanged. Although there is more than a half-point difference in air-dried brightness between the pulps, the peracid pulp suffers less heat reversion, and the oven-dried brightnesses are virtually equal. Pulp viscosity from the peracid sequence is higher than that from the control sequence.

Peracid as delignifier and brightener in TCF sulfite bleaching

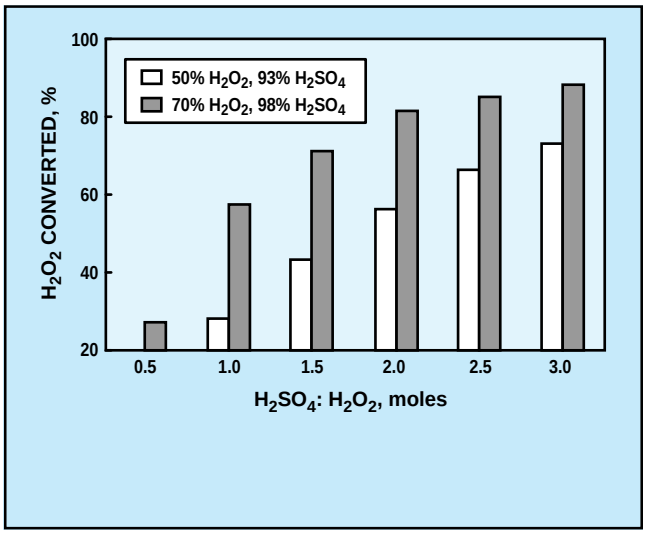
Paper-grade sulfite mills are facing the prospect of shifting to totally-chlorine-free bleaching to comply with cluster rule proposals. Ozone TCF sequences are well known from European experience but are often viewed with caution by U.S. pulp producers because of retrofit investment requirements. For that reason, some are considering the more conventional approach of chelation and hydrogen peroxide, using modified bleach plants with combined towers to obtain the longer times needed for the large hydrogen peroxide stages.

Peracids can be beneficial in this instance, as shown in **Fig. 4** and **Table V.** They illustrate brightness development and bleaching conditions for a North American sulfite softwood bleached via a Q(PSP) sequence with a long multitower P stage and a similar Q(PPxaP) sequence in which peracid is added dur-

6. Equilibrium peracetic acid: effect of mole ratio and concentration on conversion of H_2O_2 to peracid



7. Equilibrium Caro's acid: effect of mole ratio and concentration on conversion of H_2O_2 to peracid



ing the soak stage (S) to allow removing a portion of the peroxide. In this case, 1% hydrogen peroxide is replaced with 0.2% (AO as peracid) mixed peracids, making the two sequences essentially equal in cost. The peracid sequence gives three points higher brightness and higher viscosity. To provide the extended time for the large peroxide stage, the pulp is not washed between the PSP towers. Likewise, the residuals are allowed to carry through without washing in the PPxaP sequence.

Although TCF bleaching is not proposed in the cluster rules for kraft pulp, there are mills developing TCF processes on kraft for marketing reasons. One approach is to use primarily oxygen, chelation, and hydrogen peroxide to bleach these pulps. Advantages similar to those previously cited for TCF sulfite can often be achieved by using peracids to replace part of the hydrogen peroxide dose in those TCF kraft sequences.

V. Peracid as delignifier and brightener for TCF sulfite bleaching*

	Q(PSP)	*Q(PPxaP)*
P1 tower: 10% cons., 50 min, 80°C		
H_2O_2, %	2.8	2.0
NaOH, %	2.8	2.0
pH, final	11.1	11.0
Kappa no.	6.5	7.0
Brightness, % ISO	79.0	76.1
	No wash	No wash
S tower: 10% cons., 50 min, 80°C		
Pxa, % AO as peracid	-	0.2
NaOH, %	-	0.75
pH, final	11.0	6.2
Kappa no.	5.7	5.5
Brightness, % ISO	80.8	80.4
	No wash	No wash
P2 tower: 10% cons., 90 min, 80°C		
H_2O_2, %	0.6	0.4
NaOH, %	0.6	1.8
pH, final	10.9	10.7
Kappa no.	4.6	3.3
Viscosity, cp	14.6	17.0
Brightness, % ISO	84.2	87.0

*Starting pulp: Sulfite softwood, Q treated, kappa no. 15.9, 58.2% ISO, 25-cp viscosity

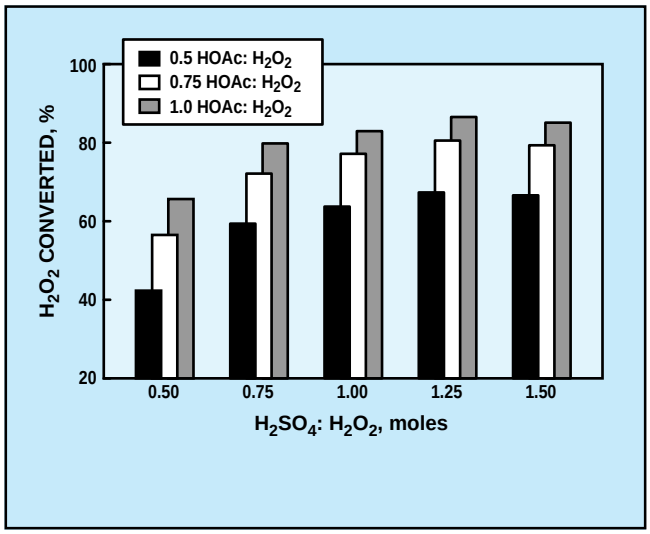
Peracids: Tools for cluster rule strategies

The previous examples illustrate that there are cases where peracids can contribute to cluster rule bleaching strategies. Several authors have presented a variety of similar results *(2–8),* and their discussions lead to the same general conclusion that the bleaching and delignifying properties of the peracids warrant their consideration for use in low-AOX, ECF, and TCF sequences.

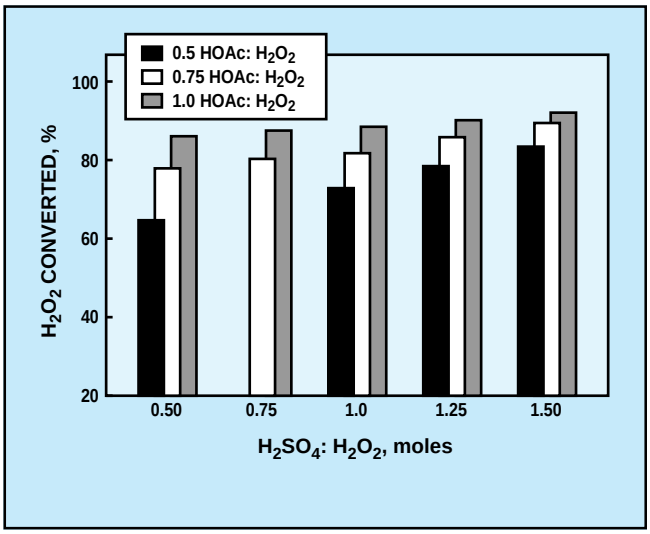
Comparing and differentiating among peracids

For those considering peracids in a strategy to address cluster rule proposals, the following choices are available: (a) peracetic [Pa, equilibrium or distilled], (b) Caro's acid [Px], or (c) mixed peracids [Pxa, an

8. Equilibrium mixed peracids: effect of mole ratios on H_2O_2 conversion—50% H_2O_2, 93% H_2SO_4, 100% HOAc



9. Equilibrium mixed peracids: effect of mole ratios on H_2O_2 conversion—70% H_2O_2, 98% H_2SO_4, 100% HOAc



VI. Bleaching conditions for Fig. 5

Fig. 5(a) *(13)*

Brownstock: kappa no. 17 southern pine, 29.8% ISO, 23-cp viscosity

Peracid stages: 0.17% peracid (AO basis), 70°C, 10% consistency, 60 min, final pH 4.5–5.5

Eop stage: 0.5% H_2O_2, 90°C, 10% consistency, 60 min, 60 psig for 15 min, final pH≈11

Fig. 5(b)

Brownstock: kappa no. 7.5 hardwood, 37.6% ISO, 26-cp viscosity

Peracid stages: 0.34% peracid (AO basis), 77°C, 11% consistency, 45 min, final pH≈6.5, no wash

Ep stage: 1.0% H_2O_2, 77°C, 11% consistency, 60 min, pH≈11

Fig. 5(c)

Brownstock: kappa no. 10.2 pine, 38% ISO, 24.3-cp viscosity

Peracid stages: 0.19% peracid (AO basis), 65°C, 10% consistency, 40 min, final pH 4.2–4.5

Eop stage: 0.5% H_2O_2, 80°C, 10% consistency, 60 min, 24 psig for 20 min, pH≈11.5

equilibrium solution of both Caro's and peracetic acids]. The balance of this paper addresses differences among these peracids, making comparisons with respect to:

- Delignifying and brightening efficiency
- Chemistry of the on-site manufacturing processes, including economics and chemical effluent load
- Operating issues for the on-site processes, including chemical safety and handling and process utility.

Emphasis is placed on the on-site processes for making the various peracids, because that is where the differences are most significant.

Delignifying and brightening efficiency

For a variety of conditions, equal peracid (equal active oxygen in peracid form or equal molar amounts of peracid) gives equal delignifying and brightening. See **Fig. 5** and **Table VI** *(13)*.

Figure 5(a), on kappa no. 17 southern pine, shows slightly more delignification and brightening by Px compared to Pxa and Pa in the two-stage sequence peracid plus an oxidative extraction stage. Figure 5(b), on low-kappa hardwood, shows Px and Pxa equal as delignifiers, but Pxa is slightly better as a brightener. Figure 5(c), on kappa no. 10 pine, shows Pa and Pxa equal as delignifiers and Pa very slightly better at brightening. In sum, we conclude that equal peracid AO gives equal performance, whether from Pa, Pxa, or Px.

The equilibrium Pa, Px, and Pxa solutions referred to in Fig. 5 and Table VI all contain active oxygen in the form of both peracid and hydrogen peroxide. To assure equal peracid AO in the bleaches, the peracid solutions were analyzed by a two-step titration to measure the

hydrogen peroxide content and the amount of peracid (expressed as active oxygen). The dose for the bleaching experiment was calculated on the basis of the peracid AO.

Since equal amounts of peracid AO, whether from Pa, Pxa, or Px, give essentially equal bleaching and delignification, other factors should be used in deciding among them.

Economics of manufacture and use in bleaching

One reasonable way to compare the various peracids is to consider the economics of making and using an equal molar amount of each. This comparison begins with the general chemical equilibrium equation:

$$H_2O_2 + \text{Acid} \leftrightarrow \text{Peracid} + H_2O$$

which is the basis for the recently proposed peracid processes *(6, 9–11)*. Shifting this equilibrium to the right to improve the conversion of H_2O_2 to peracid can be done by three methods:

- Increasing the mole ratio of acid to H_2O_2
- Increasing the concentration of ingredients
- Distilling to remove the peracid product.

Although the basic chemical equilibrium is simple, there are many cases to consider, which makes the comparison more involved. This analysis evaluates the seven cases outlined in **Table VII** and considers the equilibrium cases at varying acid-to-hydrogen peroxide mole ratios to optimize for ingredient cost per unit of peracid AO produced.

Each of these cases gives a specific yield on H_2O_2, i.e., conversion of H_2O_2 to peracids. These are shown for equilibrium peracetic. These are Caro's acid, and mixed peracids in **Figs. 6–9.** In the mixed peracid cases, there are two independent acid-to-peroxide mole ratios [H_2SO_4:H_2O_2 and acetic (HOAc):H_2O_2] that can be varied, which adds to the number of cases to be considered (see Figs. 8 and 9). Each case makes a different peracid solution containing different amounts of peracetic or Caro's acid (or both), unconverted acetic or sulfuric acid (or both), unconverted H_2O_2, and water. The amount of each can be calculated from a material balance using the starting mole ratio of ingredients, the percent H_2O_2 converted, and the concentrations of ingredients. **Table VIII,** for Caro's acid solutions, is an example of these equilibrium peracid solutions changing composition with the mole ratios and ingredient concentrations.

Distilled peracetic acid is different from the equilibrium cases in that the peracid product is removed from the reaction mass. This process is based on feeding a 1:1 mole ratio of acetic acid and hydrogen peroxide to a still and achieving a peracetic acid yield of 92% on hydrogen peroxide. The distilled peracid solution is 44.9% peracetic acid, 51.7% water, 3% acetic acid, and 0.4% hydrogen peroxide.

Comparisons hereafter among the peracid solutions are for that amount of solution containing peracetic acid, or Caro's acid, or both (Pxa), which contain the peracid AO equivalent of 1 lb of Caro's acid (i.e., on the basis of an equivalent pound of H_2SO_5).

Sodium hydroxide is included in the ingredient cost comparisons because these peracid solutions contain varying amounts of acids that require neutralization during the bleaching reaction. The analysis assumes that the peracid stage is operated to achieve a final pH of 4.5 or slightly higher, and accordingly adds NaOH to neutralize all the H_2SO_4 and half of the acetic acid present at the end of the stage. These amounts agree well with lab and mill results.

Figures 10–13 show for each case the combined cost of H_2O_2, H_2SO_4, and acetic acid ingredients, plus the cost for caustic to adjust to pH 4.5 in use. Prices used for H_2O_2 (US$ 0.46/lb) and caustic (US$ 0.1075/lb) are from *Bleaching Chemicals*, Harriman Chemsult Ltd., issue no. 54, June 8, 1994. Acetic (US$ 0.33/lb) and sulfuric acid (US$ 0.0375/lb) were taken from *Chemical Marketing Reporter*, Schnell Publishing, June 20, 1994. All are at the low end of the ranges quoted except caustic, which is the average of the low ends of spot and list quotations.

VII. Peracid process comparisons

Process	Ingredient cost and effluent load: Pa	Px	Pxa
Equilibrium: 50% H_2O_2, 93% H_2SO_4, ≈100% HOAc	x	x	x
Equilibrium: 70% H_2O_2, 98% H_2SO_4, ≈100% HOAc	x	x	x
Distillation	x	N/A	N/A

Increasing hazards potential

Decreasing ingredient cost

VIII. Composition example of equilibrium peracid solutions

Mole ratio	Concentration, %		Composition of Caro's acid solution, %			
H_2SO_4:H_2O_2	H_2SO_4	H_2O_2	H_2SO_5	H_2SO_4	H_2O_2	H_2O
2.5:1.0	98	70	32.5	54.5	1.5	11.5
1.5:1.0	98	70	41.0	39.0	5.0	15.0
1.5:1.0	93	50	21.5	46.5	8.5	23.5

IX. Peracid process comparisons

Process	Ingredient cost, $/lb of equivalent H_2SO_5		
	Pa	Px	Pxa
Equilibrium:			
50% H_2O_2	0.78	0.61	0.51
70% H_2O_2	0.58	0.41	0.43
Distillation	0.36	N/A	N/A

Increasing hazards potential

It is clear from Figs. 10–12 that the ingredient costs to make and use peracids on-site can vary significantly, depending on the peracid made and the recipe and process used. Because the yield on each ingredient changes with the recipe and process, these differences are also a function of the relative prices of the ingredients used. These price relationships change independently of one another as supply and demand of the various ingredients fluctuate.

With this set of published prices, economics favor mixed peracids if 50% hydrogen peroxide is used, and Caro's acid and mixed peracids are about equal if 70% peroxide is used. Peracetic acid does not compare favorably unless the distillation process is used. See **Table IX.**

Apart from the ingredient costs, however, there are other factors to consider in selecting a peracid. Safety and effluent chemical loads, alluded to in Table VII, are discussed below.

Chemical safety and handling

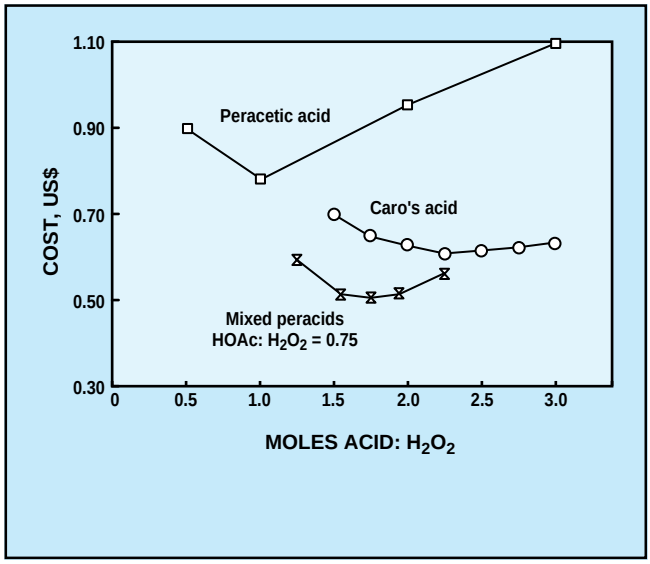
Any time a new chemical or process is introduced at a site, there are new hazards to be aware of and manage to assure the continued health and safety of employees, the community, customers, and the environment. In that light, the peracid processes appear in Table IX in order of increasing hazard potential. They all require understanding and managing the hazards of using and handling peracid, a stronger oxidizer than hydrogen peroxide. There is no differentiating among them in that respect. However, comparing them with respect to other potential hazards does reveal differences.

Equilibrium processes using 50% H_2O_2. Virtually all mills currently use 93% H_2SO_4, and many mills also use 50% hydrogen peroxide, the ingredients for Caro's acid. Thus Px has the lowest level of added hazard because it introduces no new chemicals, except the product. Pxa and Pa raise safety concerns slightly in that they require one new chemical on site, glacial (100%) acetic acid. It is not a particularly hazardous material, but it is a weak acid and has a strong vinegar odor that must be contained for good industrial hygiene. It freezes at 62°F and would require heated storage and transfer lines, which is a handling rather than safety issue.

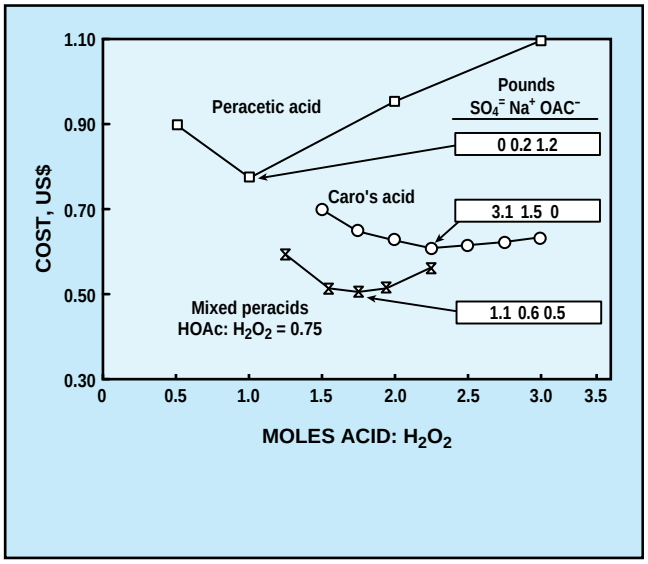
Equilibrium processes using 70% H_2O_2. In addition to the previously mentioned items, these processes have significantly increased safety hazards in that they require storage and handling of 70% rather than 50% hydrogen peroxide. Although both can be stored and handled safely, the danger of eye or skin damage is greater on exposure to 70%. Spontaneous combustion is more likely to occur if combustible materials are accidentally exposed to 70% hydrogen peroxide. With 70% hydrogen peroxides potential consequences of decomposition initiated by contamination are also significantly greater. In concentrations above 65% H_2O_2, there is insufficient water present, or formed, to remove the heat of decomposition by vaporization. This can lead to self-accelerating decomposition with the potential of a violent pressure rupture of the storage vessel. In recognition of these added potential hazards, storage and handling facilities for 70% hydrogen peroxide require additional safety engineering. Also, the 70% version is more highly regulated at both the local and federal levels.

Distillation process for peracetic acid. This is a continuous process in which acetic acid and hydrogen peroxide are fed to the reactor (still pot). Peracetic acid and water, along with some unreacted acetic acid and a trace amount of hydrogen peroxide, are removed overhead under vacuum. Sulfuric acid, the process catalyst, remains in the still pot and is not volatilized. However, a small amount of sulfuric acid must be added as makeup, since the process requires a purge to pre-

10. Ingredient cost of equilibrium peracids per lb H_2SO_5 equivalent—50% H_2O_2, 93% H_2SO_4, 100% HOAc



11. Peracid ingredient cost and effluent load per lb H_2SO_5 equivalent—50% H_2O_2, 93% H_2SO_4, 100% HOAc



vent accumulation of metal ions in the reactor. The purge is necessary to avoid excessive decomposition of the hydrogen peroxide and peracetic in the still bottoms *(14)*.

A homogeneous azeotrope of peracetic acid (56.5%) and water (43.6%), boiling at 34°C and 45 mm Hg has been reported in the literature *(15)*. This solution undergoes explosive autodecomposition at approximately 80°C, but the autodecomposition temperature may be lower if the sample is contaminated with metal ions. Safe operation of the peracetic acid distillation process requires:

- Close control of the process to prevent a low-temperature decomposition (< 60°C) from accelerating to the explosion temperature (80°C)
- The elimination or minimization of decomposition catalyzed by metal ions
- The use of a properly sized relief device.

Certain mixtures of acetic acid and concentrated hydrogen peroxide (> 50%) are detonable, and for safety, the process is normally run with 35–50% hydrogen peroxide. Precautions must be taken, however, to ensure that misoperation of the still does not result in forming a detonable mixture of concentrated peroxide and acetic acid. For example, if the sulfuric acid catalyst concentration in the still drops to a low level, the reaction between acetic acid and peroxide slows. Since little peracetic acid is produced under these conditions, operation of the still results primarily in removal of water overhead. The hydrogen peroxide feed to the reactor thus becomes concentrated and can form a detonable mixture with the added acetic acid. Similarly, if the acetic acid flow to the reactor is interrupted while distillation is in progress, water removal continues, and the peroxide becomes concentrated. If acetic acid flow is then restored, the still reaction mass may enter the detonable range.

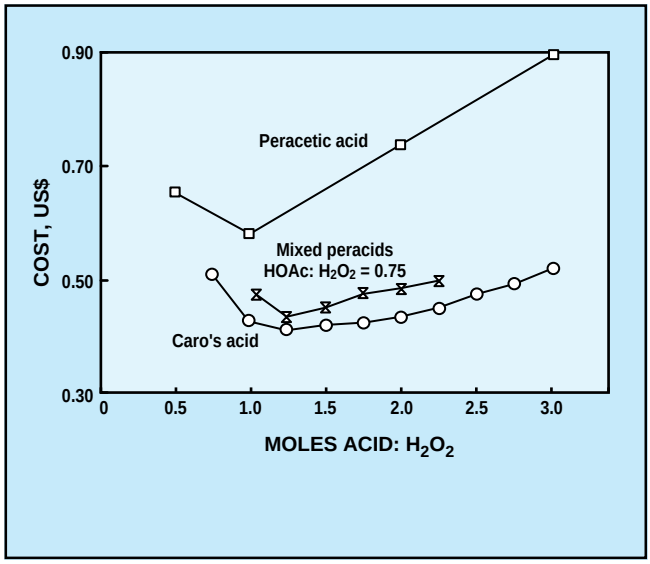
Mixtures of peracetic acid and acetic acid, when concentrated, can also be detonated by shock. The sample's sensitivity to detonation is dependent on its temperature and concentration. Literature data show that the higher the peracetic acid concentration, the lower its detonation temperature *(15)*. Commercial samples of peracetic acid are normally less than 40% in peracetic acid and considered to be insensitive to shock at ambient temperature.

Chemical effluent load

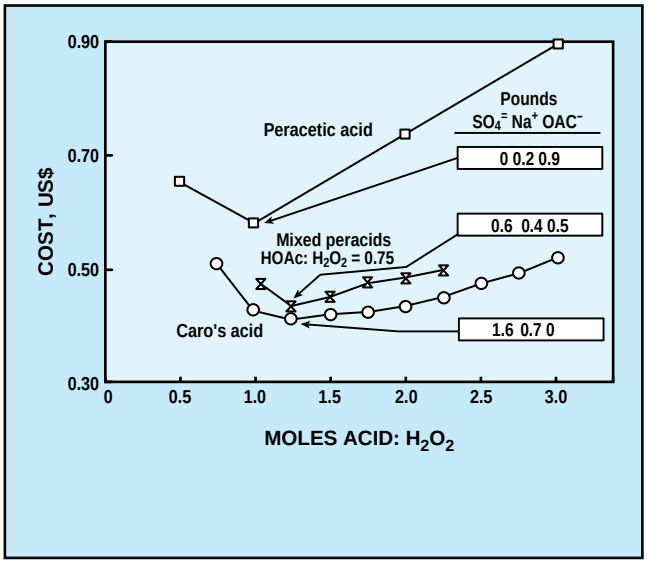
It is also instructive to consider chemical effluent loads introduced by each process used to make the peracid, because they differ significantly and may represent further costs, credits, or operating issues. We briefly review three chemicals present in different amounts at the end of a peracid bleach stage; these must be considered in light of effluent-handling issues. They are sulfate ion from the spent Caro's and unconverted sulfuric acid, acetate ion from spent peracetic and unconverted acetic acid, and sodium ion from the caustic used to adjust the pH for bleaching.

If the filtrate from the peracid stage is to go to recovery, as might be the case for a mill considering eventual bleach plant closure, the effluent load is obviously a factor in the sulfur and sodium balance. On the other hand, if the filtrate is to be sewered, sulfate and sodium may not be high-priority items, but the mill must be prepared to treat the biological oxygen demand (BOD) load represented by the acetate, i.e., about 0.7 lb BOD/lb acetate. Fig-

12. Ingredient cost of equilibrium peracids per lb H_2SO_5 equivalent—70% H_2O_2, 98% H_2SO_4, 100% HOAc



13. Peracid ingredient cost and effluent load per lb H_2SO_5 equivalent—70% H_2O_2, 98% H_2SO_4, 100% HOAc



ures 11 and 13 show the effluent loads expected for a bleach sequence done with the least expensive case of each of the peracid processes. Sulfate ($SO_4^=$), sodium (Na^+), and acetate (OAc^-) are expressed as lb/lb of H_2SO_5 equivalent initially charged to the bleach stage, and are compiled along with the corresponding ingredient cost/lb H_2SO_5 equivalent in **Table X.**

The completed Table X is a framework for considering three factors (safety, ingredient costs, and effluent loads) that could influence a mill's choice among the peracids. The equilibrium cases using 50% H_2O_2 introduce the fewest new safety issues, and in this category mixed peracids have the lowest ingredient cost. If a mill could not tolerate the half-pound of acetate in the Pxa effluent, it might opt for the higher-cost Px. Likewise, a low tolerance for sulfate effluent and an ability to manage a high acetate effluent could drive the decision toward Pa, which is a still-higher cost.

At the next level of new hazards, equilibrium cases using 70% H_2O_2, peracetic acid is in relatively the same position; there is little to recommend it except low tolerance for sulfate. Px and Pxa have approximately equal ingredient costs that are still significantly lower than Pa. As it was for the 50% cases, the sulfate effluent of Pxa is about one-third that of Px, and the sodium load is about one-half. Provided the mill could handle the half-pound of acetate, the choice between Px and Pxa would probably hinge on whether these sulfur and sodium levels were considered to be a credit or a cost. The effluent load is proportional to peracid dose, so that credit or cost question could also depend on the peracid dose(s) contemplated for the bleach sequence(s).

For the three peracids we are considering, the distillation process can only be applied to peracetic. If a mill is comfortable with the potential for detonation hazards of operating the still, distillation can bring Pa into a favorable position. Ingredient costs drop substantially and are the lowest of all cases for the particular set of ingredient prices used in this analysis. However, that position may erode on a full-cost basis, as investment and fixed costs would probably be higher for distillation than for the simpler equilibrium processes. If sulfur and sodium in effluents are considered liabilities, this option is the most favorable, provided the modest acetate load is manageable.

Process utility issues

In addition to the options in the previous section based on process chemistry differences, there are also choices among the peracids that originate from process engineering differences and raise bleach plant utility issues. At least three classes of processes have been described for the peracids.

- The distillation process to make nonequilibrium peracetic acid as described above (Process 1)
- A mixing-only process for Caro's acid that pumps hydrogen peroxide and sulfuric acid through a mixing tee to form the peracid and immediately injects the flow into pulp stock, thereby quenching the heat of mixing and simultaneously starting the bleaching (Process 2)
- A mixing-cooling process for Caro's acid, peracetic, or mixed peracid that removes the heat of mixing and reaction for these products and stores an equilibrium peracid solution for pumping to the bleach plant (Process 3).

Process 2 runs with no product inventory, desirable in that it eliminates safety considerations about storing the peracid. However, no inventory also means that if the peracid process shuts down unexpectedly (ingredient pump failure or mixing tee problem, for example), the bleach plant could be shut down. Also, if the peracid quality suffers cyclic variations (ingredient flow ratio, for example), so does the bleaching. It is also likely that duplicate peracid manufacturing operations will be required if a mill must add the peracid to more than one bleach line, or to more than one point in a single line. Processes 1 and 3 operate with a peracid inventory and would not be subject to these issues.

X. Peracid process comparisons

Process		Ingredient cost and effluent load, per lb H_2SO_5 equivalent		
		Pa	*Px*	*Pxa*
Equilibrium (50% H_2O_2)	Cost, $/lb	0.78	0.61	0.51
	lb $SO_4^=$	0	3.1	1.1
	lb Na^+	0.2	1.5	0.6
	lb OAc^-	1.2	0	0.5
Equilibrium (70% H_2O_2)	Cost, $/lb	0.58	0.41	0.43
	lb $SO_4^=$	0	1.6	0.6
	lb Na^+	0.2	0.7	0.4
	lb OAc^-	0.9	0	0.5
Distillation	Cost, $/lb	0.36	N/A	N/A
	lb $SO_4^=$	0	N/A	N/A
	lb Na^+	0.1	N/A	N/A
	lb OAc^-	0.6	N/A	N/A

Increasing hazards potential

Experimental

Caro's acid was prepared by adding sulfuric acid to hydrogen peroxide while maintaining the reaction temperature at 30–35°C. The acid was then analyzed prior to use to determine its active oxygen content using the dual titration described later. The Caro's acid was used as the starting material for Pxa, which was made fresh before use. Caro's acid remained essentially unchanged in its assay for several weeks when refrigerated.

About 0.3–0.5 g of the Caro's acid was added to a 500-mL Erlenmeyer flask containing 100 mL of distilled water and 10 mL of 20% sulfuric acid. One to three drops of Ferroin indicator was then added to the flask (solution turns reddish-orange in color), and it was titrated immediately with 0.1 N ceric ammonium sulfate to a pale blue endpoint. Approximately 10 mL of 25% potassium iodide was then added to the flask, and the mixture was titrated with 0.1 N sodium thiosulfate until the dark reddish color of iodine began to fade. A starch indicator, 2–3 mL, was added at this point, and the titration was continued until the dark blue color changed to a pale reddish-orange color endpoint. The concentration of H_2O_2 and peracid active oxygen were determined by using the following formula:

$$\% H_2O_2 = (V_{ceric} \times 0.1 \times 1.7)/\text{Sample weight} \quad (1)$$

$$\% AO = (V_{thio} \times 0.1 \times 0.8)/\text{Sample weight} \quad (2)$$

Pxa samples were prepared by adding the required amount of glacial acetic acid to the cold Caro's acid, prepared as described above, and analyzed using the procedure described for Caro's acid. Equilibrium peracetic acid was prepared by adding glacial acetic acid to hydrogen peroxide containing the sulfuric acid catalyst. The mixture was then warmed to 45°C, held at this temperature for two hours, and stored overnight in a refrigerator to allow the mixture to reach equilibrium. The product was then assayed as above.

Bleaching experiments for peracids and all other stages, except Eop and oxygen delignification, were performed in sealed plastic bags placed in thermostatically controlled water baths to maintain bleach temperatures. The Eop and oxygen delignification stages were done in a stainless steel pressure reactor. Unless otherwise indicated, chemical charges are weight percent chemical (100% basis) on oven-dry pulp, and each stage was followed by a wash.

Conclusions and recommendations

Caro's acid, mixed peracids, and equilibrium and distilled peracetic acid are four similar strong oxidizing solutions that have been proposed for manufacture at mills needing nonchlorine oxidizers. They have similar delignifying and brightening properties that justify their consideration by mills preparing bleaching strategies to meet cluster rule proposals. They can be used in response to cluster rule requirements for AOX reduction, hypochlorite elimination, or TCF bleached sulfite pulps.

Although they have similar oxidizing properties, the peracid solutions are different in several important ways that could influence a mill's choice of which solution to use. Site-specific conditions, such as

relative differences in delivered prices of ingredients, can influence which peracid (or which recipe for a given peracid) has the lowest cost/lb of AO. There are different safety issues associated with equilibrium peracids from 50% and 70% H_2O_2 and from distilled peracetic acid. Sulfur, sodium, and BOD in the peracid stage effluent could be deciding factors, depending on a mill's ability to manage each. These and other differences should be reviewed before deciding which peracid to use.

Literature cited

1. Cael, J. J., U.S. pat. 4,404,061 (Sept. 13, 1983).
2. Song, J., Chang, H-m., and Jameel, H., *Proceedings 7th International Symposium on Wood and Pulping Chemistry, Vol. I,* Beijing, 1993, p. 34.
3. Springer, E. L. and McSweeny, J. D., *Tappi J.* 76(8): 194(1993).
4. Allison, R.W. and Kim, G. M., *CPPA 1994 International Pulp Bleaching Conference–Poster Preprints*, CPPA, Montreal, p. 121.
5. Anderson, J. R., Webster, J. R., Amini, B., *et al., Proceedings 47th Appita Annual General Conference,* Appita, Rotarua, New Zealand, 1993, p. 461.
6. Devenyns, J., Desprez, F., and Troughton, N. A., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 341.
7. Basta, J., Holtinger, L., Lundgren, P., *et al., Proceedings 1994 Non-Chlorine Bleaching Conference,* Miller Freeman, San Francisco, Paper No. 11.3.
8. Francis, R. C., Troughton, N. A., Zhang, X. Z., *et al., CPPA 1994 International Pulp Bleaching Conference–Poster Preprints,* CPPA, Montreal, p. 165.
9. Geng, Z. P., Chang, H-m., Jameel, H., *et al., TAPPI 1993 Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 357.
10. Seccombe, R., Hill, R., Martens, H., *et al., Proceedings 1994 Non-Chlorine Bleaching Conference,* Miller Freeman, San Francisco, Paper No. 11.4.
11. Meier, J., Arnold, G., Choiniere, R., *et al.,* U.S. pat. 5,141,731 (Aug. 25, 1992).
12. Lane, J., McDonogh, C. F., and Woods, S. E., "Peroxyacid Manufacture," Patent application, WO 92/07791 (May 14, 1992). 1992).
13. Geng, Z. P., Chang, H-m., Jameel, H., *et al., CPPA 1994 International Pulp Bleaching Conference–Poster Preprints,* CPPA, Montreal, p. 25.
14. "The Manufacture of Aqueous Peracetic Acid from Hydrogen Peroxide and Acetic Acid," Pilot plant report, Unpublished DuPont Co. report.
15. Phillips, B., Starcher, P. S., and Ash, B. D., *J. Org. Chem.* 23: 1823(1959).

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