

# Hydrogen peroxide and caustic soda: Dancing with a dragon while bleaching

PETER W. HART, CARL HOUTMAN, AND KOLBY HIRTH

**ABSTRACT:** When hydrogen peroxide is mixed with caustic soda, an auto-accelerating reaction can lead to generation of significant amounts of heat and oxygen. On the basis of experiments using typical pulp mill process concentration and temperatures, a relatively simple kinetic model has been developed. Evaluation of these model results reveals that hydrogen peroxide-caustic soda systems are extremely sensitive to hydrogen peroxide:caustic soda ratio, transition metal contamination, and temperature. Small changes in initial conditions can result in a close system becoming explosive. Analysis of model results was used to develop guidelines for safer application of hydrogen peroxide in a mill setting.

**Application:** Because peroxide at 10% cannot generate an explosive mixture with sodium hydroxide, mills that either install new or retrofit bleaching systems should consider installing a dilution system that will take the peroxide from the storage concentration of 50% to 10% before introduction into the mixer.

Hydrogen peroxide is an environmentally compatible bleaching chemical that has been employed in kraft mills for many years. As part of a bleaching sequence, hydrogen peroxide brightens and provides brightness stabilization, if used as the last stage in a multistage bleach plant [1-4]. Because hydrogen peroxide bleaching does not delignify fibers, it does not produce as many soluble by-products as other popular bleaching chemicals; thus, it can reduce organic load to wastewater treatment plants.

Hydrogen peroxide is delivered to pulp mills via tank truck or railcar. Truck deliveries are near 50% concentration [5]. Railcar deliveries may be either at 50% or 70% concentration. If a mill receives hydrogen peroxide deliveries at 70% concentration, it is routinely diluted to 50% concentration as it is unloaded. Thus, industrial-strength hydrogen peroxide employed in kraft pulp bleaching is generally near 50% concentration.

Under proper storage conditions, hydrogen peroxide decomposes at a rate of about 1% per year [6]. Traces of transition metals (e.g., iron, copper, and manganese) increase hydrogen peroxide decomposition [7], and suppliers add stabilizers to sequester these metals. Fifty-percent-concentration hydrogen peroxide solutions represent major safety hazards, such as skin burns; eye injuries; potential for rapid pressurization within tanks, pipes, pumps, and/or storage vessels; potential for fire due to formation of oxygen during decomposition; hydrogen peroxide-organic vapor phase explosions; and runaway decomposition [8-11].

During startup conditions, fires resulting from the reaction of hydrogen peroxide with partially dried pulp on standpipe walls have been reported. Industrial-strength hydrogen peroxide fires are extremely dangerous because they provide a

ready source of oxygen; thus, typical extinguishing technology that uses exclusion of oxygen as a mode of action (e.g., foams or dry powders) is much less effective.

Runaway decomposition of hydrogen peroxide has resulted in catastrophic events in several mills over the last 15 years. Two bleach plants experienced pump explosions when hydrogen peroxide came into contact with caustic soda (NaOH) in the absence of pulp and resulted in serious injuries [12,13]. Both mills had been using 50%-concentration hydrogen peroxide without incident for several years.

Other incidents, one in Europe and one in North America, resulted from rapid decomposition within a storage tank when an organic chelant was mistakenly mixed with hydrogen peroxide [8,14]. In those cases, the explosions were likely caused by a combination of alkaline-catalyzed decomposition and rapid oxidation of an organic chemical.

Alkali-catalyzed decomposition of hydrogen peroxide follows second-order reaction kinetics, as shown in Eq. (1) [15]. The rate of decomposition depends on the concentration of both hydrogen peroxide (HOOH) and its conjugate base (HOO<sup>-</sup>):

$$dP/dt = -2k(\text{HOOH})(\text{HOO}^-) \quad (1)$$

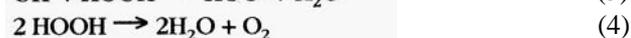
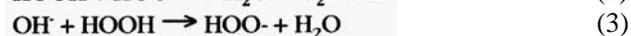
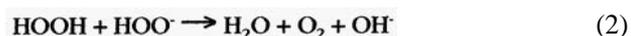
In Eq. (1), P is total hydrogen peroxide concentration (i.e.,  $P = [\text{HOOH}] + [\text{HOO}^-]$ ) and t is time. Note that the 2 is due to the consumption of two moles of hydrogen peroxide for every mole of reaction. Makkonen reported an apparent rate of  $8 \times 10^3 \text{ L/mol/s}$  at  $45^\circ\text{C}$  [14]. The apparent rate follows the Arrhenius theory with an activation energy of  $54.8 \text{ kJ/mol}$  [15]. Because the decomposition from alkaline catalysis cannot be



## BLEACHING

completely separated from decomposition due to trace transition metals [16], the interpretation of these data is difficult. As examples, Makkonen measured slower decomposition rates for reactions stabilized with magnesium or silicate [15], and Galbacs and Csanyi reported rates as low as  $10^{-6}$  L/mol/s using extreme methods to minimize inorganic contamination [16].

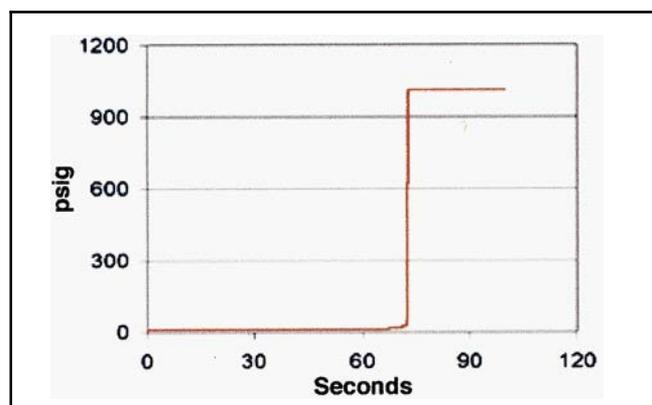
The net reaction for hydroxide ion-catalyzed decompositions produces two moles of water and one mole of oxygen for every two moles of hydrogen peroxide, shown as Eqs. (2)-(4):



The estimated activation energy for the rate-limiting reaction (Eq. [2]) is 110 kJ/mol [16].

Because bleaching efficiency is important for process economics, many studies of transition metal-catalyzed hydrogen peroxide decomposition have been published [17-19]. Unfortunately, a simple set of reactions cannot be written for iron-catalyzed decomposition. Mechanisms involving various chain reactions, radicals, reduced iron intermediates, and iron complexes have been written for the iron-catalyzed decomposition. The precise details are still the subject of active debate. The net reaction for iron-catalyzed decomposition, however, is likely the same as the alkaline decomposition (Eq. [4]), but the activation energy is likely significantly lower, about 54 kJ/mol [15].

Our previous kinetic model, developed from Makkonen's data [15], indicated that runaway decomposition may be the cause of the explosions at two chemical pulp mills [20]. It also provides a reason why chemical-pulp bleach plants tend to experience more catastrophic events than mechanical pulp mills. One prediction of this model was a delay between mixing and onset of a rapid decomposition. **Figure 1** shows a prediction of pressure resulting from mixing 25 L of 50 wt% hydrogen peroxide with 25 wt% sodium hydroxide in a vessel with a restricted vent. A limitation of this previous work was



1. Dynamic model prediction of alkaline decomposition of hydrogen peroxide in a vented mixing vessel. Conditions were 25 L of 50 wt% hydrogen peroxide with the addition of 25 wt% caustic soda [20].

	Hg Cell	Membrane	ET
NaCl	<10 ppm	<30 ppm	1.0 wt%
NaClO <sub>3</sub>	0.5 ppm	3 ppm	0.15%
Na <sub>2</sub> CO <sub>3</sub>	0.02 wt%	0.03 wt%	0.1 wt%
Na <sub>2</sub> SO <sub>4</sub>	10 ppm	15 ppm	0.01 wt%
Iron	<1 ppm	1–5 ppm	5–10 ppm

1. Typical concentrations of contaminants in commercial caustic soda [23].

that we extrapolated our kinetic model well beyond the experimental range of temperatures and concentrations and thus, errors could be substantial [11, 20]. The goal of the work described here is to conduct experiments with chemical concentrations and temperatures similar to bleach plant operating or startup conditions and then develop models without excessive extrapolation.

## EXPERIMENTAL

The experiments described here were conducted with extreme caution. In all cases, the hydrogen peroxide and sodium hydroxide were mixed in open vessels surrounded by running water. The operator wore a face shield, rubber gloves, and a full apron. The injection of the sodium hydroxide was accomplished by a syringe connected to 2 m of Teflon tubing, which allowed the operator to be away from the vessel during the mixing. If one is considering repeating these experiments, similar precautions are strongly recommended.

For all experiments, commercial hydrogen peroxide (Hydrite Chemical; Brookfield, WI, USA) was used without further purification. Using iodometric titration, a concentration of 48% hydrogen peroxide [21] was determined.

Three grades of commercial caustic soda were obtained from PPG Industries (Lake Charles, LA, USA): mercury (Hg) cell, membrane, and ET (diaphragm). They represent products from three manufacturing methods [22]. Each of these types of caustic soda likely has different concentrations of contaminants, as shown in **Table I** [23].

### Mercury-cell caustic soda

To produce Hg-cell caustic soda, mercury is used as the cathode for the electrolysis of sodium chloride (NaCl) to produce sodium amalgam that is reacted with deionized water to produce a sodium hydroxide solution. A 50 wt% NaOH solution is produced directly without any additional evaporation. The Hg-cell process produces the highest-purity caustic soda commercially available.

### Membrane-grade caustic soda

The membrane-cell process produces medium-purity caustic soda. It uses a selective membrane during the electrolysis of sodium chloride. Sodium ions diffuse across the membrane to the cathode while keeping chlorine gas and salt brine in

µg/g	Hg Cell	Membrane	ET	Limit of Quantitation
Co	nd	nd	nd	0.04
Cr	nd	nd	nd	0.02
Cu	nd	nd	nd	0.05
Fe	0.20	0.67	7.0	0.04
Mn	nd	nd	nd	0.04
Ni	nd	nd	nd	0.01
Zn	nd	0.16	nd	0.08
nd = not detected				

## II. Trace metal concentration for the caustic soda samples used in this study.

another compartment. Sodium metal is reacted with purified water to produce caustic soda. The solution produced by the membrane cell process is 33-35 wt% NaOH. The concentration is raised to 50 wt% solution by evaporation. The ion-selective membranes result in relatively low impurity levels. However, small quantities of salts do migrate across the membrane and are concentrated during evaporation to a level of 75-100 ppm depending upon membrane condition and type.

### Diaphragm (ET)-grade caustic soda

The least-pure form of commercially available caustic soda is diaphragm- or ET-process soda. This process uses asbestos or asbestos substitutes to separate the coproducts caustic soda and chlorine during the electrolysis of sodium chloride. The diaphragm cell produces weak cell liquor that contains 12-14 wt% NaOH and roughly the same concentration NaCl salt. The cell liquor is subsequently evaporated in a multieffect evaporation process to a final concentration of 50 wt% NaOH. Excess salt is crystallized and filtered through the evaporation process for subsequent reuse or recycle. This process produces the lowest-quality electrochemical caustic soda solutions.

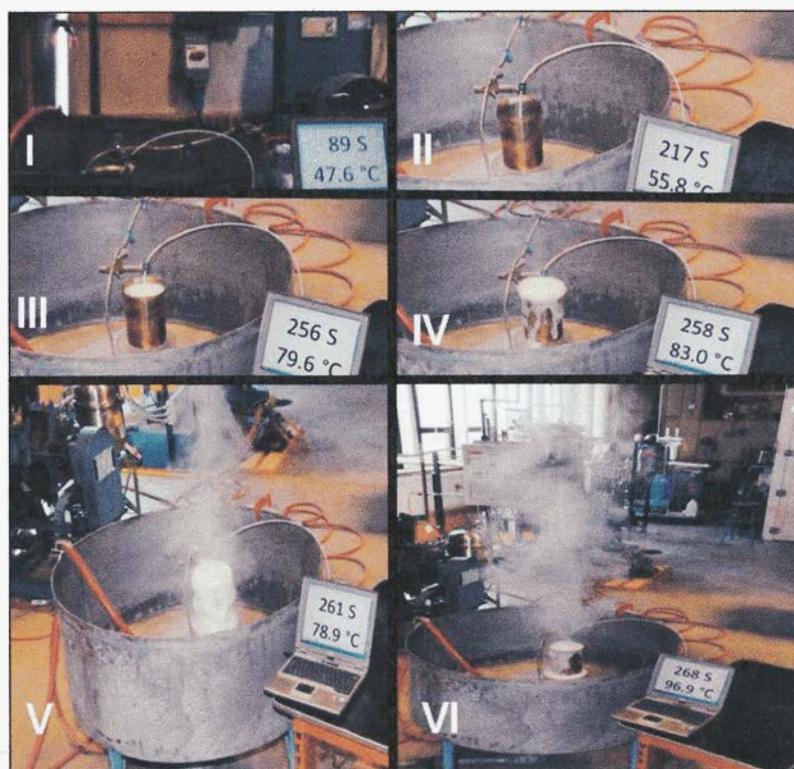
Table II shows the specific analysis results for trace metal contamination of the caustic soda samples employed in this work using ICP-OES (inductively coupled plasma-optical emission spectrometry). Samples of all three caustic grades were surveyed for the presence of metal contamination and were analyzed quantitatively for several metals. Caustic samples were prepared by neutralization with hydrochloric acid and dilution to 1:25. Standards were prepared by serial dilutions of 20 ppm stock solutions with equimolar NaCl. A Horiba Ultima II spectrometer (Irvine, CA, USA), equipped with the whole spectrum WIN-Image survey-mode software and the Analyst quantitative software, was

used under standard conditions and with argon humidification. Table II shows only iron and zinc present above the methods detection limit of quantitation. For most of the elements, the concentration is below the detection limit of the method. Using a colorimetric analysis [24], the iron composition was also determined to be 0.2, 0.5, and 2.9 ppm for Hg cell, membrane, and ET caustic soda, respectively. The deionized water employed for this work was also analyzed for iron and determined to be below 0.1 ppm, the detection limit of the method.

### Visual demonstration

For the purposes of illustrating the decomposition of hydrogen peroxide, 200 mL of commercial 48 wt% hydrogen peroxide was added to a 2-L stainless-steel beaker. The beaker was placed on a glass stand inside a much larger steel tank with running water diluting any overflow before going to a drain. A separate clamp was used to secure a K-type thermocouple and Teflon tubing connected to a syringe in the beaker. At time 0 s, 30 mL of 25 wt% Hg-cell caustic soda was injected into the hydrogen peroxide. Time and temperature were displayed using an in-house written data acquisition program driving a National Instruments (Austin, TX, USA) data acquisition board.

Figure 2 shows progress of the hydrogen peroxide-caustic soda reaction via a series of still frames taken over 268 s.



2. Sequence of photos taken during hydrogen peroxide decomposition. The reaction time and temperature are displayed on the computer screen. Mercury-cell grade caustic soda, 30 mL, was injected into 260 mL of hydrogen peroxide at 0 s. The initial mixture temperature was 45°C. The temperature slowly rises over 4 min and then rapidly accelerates over 5 s. The rapid release of energy is demonstrated by the large steam plume.

## BLEACHING

The initial temperature of the combined reaction mixture was 45°C. After 89 s, the mixture temperature had risen to 47.6°C (frame I). The temperature continued to slowly rise, reaching 55.8°C after 217 s (frame II). At 256 s (frame III), the reaction appears to accelerate and rapid oxygen gas evolution turns the reaction mixture from a clear liquid into a frothy mixture. After 2 s more (frame IV), the mixture is overflowing the reaction vessel and the temperature continues to rise. Two seconds after that (frame V), the gas evolution and heating is so rapid that a steam plume can be seen. Finally, (frame VI) after 268 s of reaction, the temperature has reached 96.9°C and the reaction is beginning to subside. In summary, after a slow temperature rise over 4 min, the reaction dramatically accelerates over less than 5 s and generates large amounts of steam and oxygen. Clearly, if this reaction occurred in a closed vessel, an explosion would have been likely.

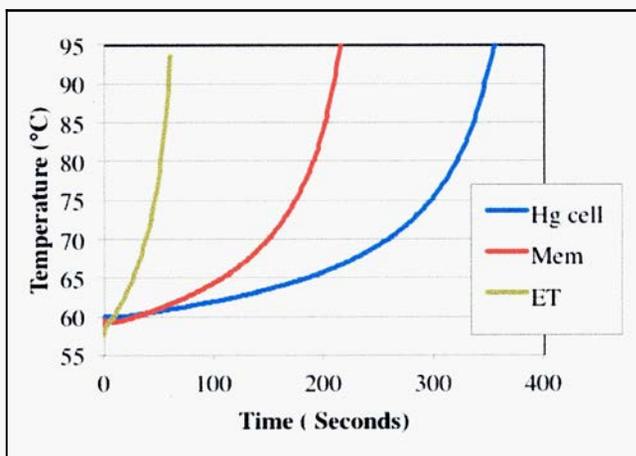
### Calorimeter experiments

Experiments similar to the visual experiments were conducted with commercial-grade 48 wt % hydrogen peroxide, but the stainless steel beaker was replaced with a glass vacuum dewar to reduce the heat loss and reactions caused by the stainless-steel container. A Teflon-coated, motor-driven stirrer operating at 100 rpm was used to ensure complete and rapid mixing. The three grades of caustic soda were used after dilution to 25% concentration with deionized water. For each experiment a measured amount of hydrogen peroxide, approximately 200 g, was mixed with various amounts of diluted caustic soda, 35–85 g. Temperature data were collected at approximately 8 Hz with the same computer system described previously.

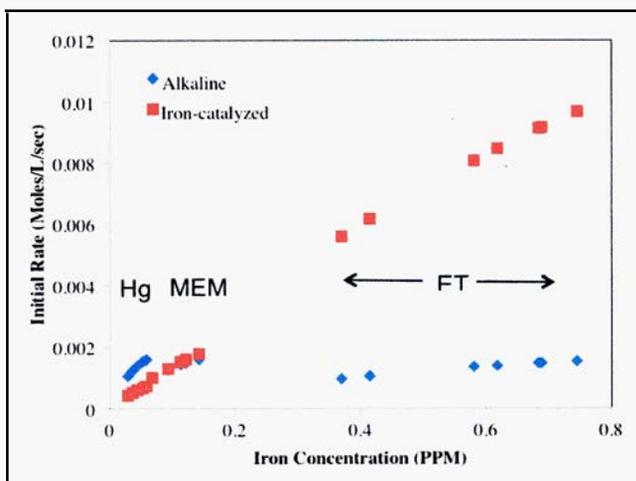
## RESULTS

calorimetric experiments were performed at various ratios of hydrogen peroxide-to-caustic soda concentrations. Typical data are shown in Fig. 3. While the concentrations were similar, the temperature rises appear to occur at different rates, with the caustic containing the highest iron concentration (ET) being the fastest.

The results from 21 similar trials were used to estimate the rate constants for alkali- and iron-catalyzed decomposition. The rate equations were integrated using a fifth-order Runge-Kutta method implemented in Microsoft Excel. Two parallel reactions with different activation energies were assumed, and the Solver function in Excel was used to optimize the kinetic parameter values to minimize the squared error between the model and the data for all the experiments at the same time. A single set of kinetic parameters was able to fit the data set spanning all 21 experiments, a total of 7500 temperature measurements, with an average error of 0.5°C. The best fit of the data was obtained when the activation energies of the alkali- and iron-catalyzed decomposition were set to 108 and 51.7 kJ/mol, respectively. The model also accounted for the heat carried away by the evaporation of water from the mixture.



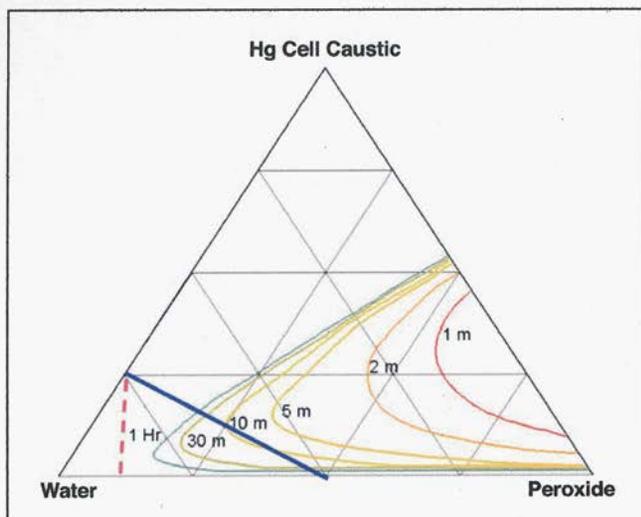
3. Temperature versus time for a mixtures of 35g of 25% caustic soda and 200g of 48% hydrogen peroxide.



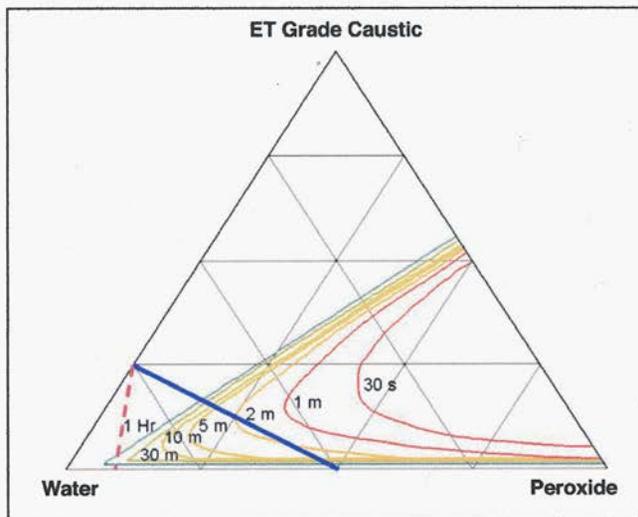
4. Initial rate at 50°C for various mixtures of hydrogen peroxide and caustic soda.

The results of the model can be used to estimate the initial reaction rate at 50°C due to both the alkali- and iron-catalyzed reactions. The differences among the various grades of caustic soda become apparent. Inspection of Fig. 4 shows that for Hg-cell caustic soda, approximately 70% of the initial rate is due to the alkali-catalyzed mechanism. For ET-grade caustic soda, the iron-catalyzed pathway dominates.

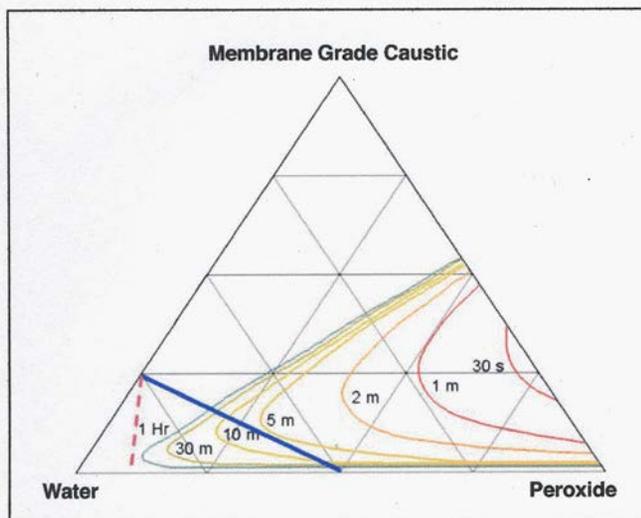
In a triangle diagram, Figs. 5–7, all possible compositions of a three-component mixture can be represented. Each vertex represents a different pure component. For example, progressing left to right along the base represents a progression from pure water to pure hydrogen peroxide, with the mid-point representing a 50:50 mixture. Because the kinetic parameters for the two reactions were estimated from the calorimetric experiments and the iron concentration is known, it was possible to determine the time for a reaction mixture, with a particular composition, to reach 100°C. The results of this calculation, assuming an initial temperature of 50°C, are represented as time contours on triangle diagrams (Figs. 5–7). For example, Fig. 5 shows that compositions enclosed by the



**5. Reaction model results for mercury-cell grade caustic soda.** For a mixture starting at 50°C, the contours represent the time required to reach 100°C. The blue line represents the operating line for typical mill operation. The pink line is our proposed safer operating line. Graph axes are explained in the text.



**7. Reaction model results for ET-grade caustic soda.** For a mixture starting at 50°C, the contours represent the time required to reach 100°C. The blue line represents the operating line for typical mill operation. The pink line is our proposed safer operating line. Graph axes are explained in the text.



**6. Reaction model results for membrane-grade caustic soda.** For a mixture starting at 50°C, the contours represent the time required to reach 100°C. The blue line represents the operating line for typical mill operation. The pink line is our proposed safer operating line. Graph axes are explained in the text.

red contour, high hydrogen peroxide concentrations, will boil in less than a minute and as more water is added (i.e., moving toward the water vertex), the time to boiling goes up.

Turning to bleach plant operation, all mixtures of 25 wt% caustic soda and 50 wt% hydrogen peroxide will be somewhere on the thick blue lines on these triangle diagram. These lines represent the operating line when there is no pulp flaving in the system. Notably in all three cases, the operating line enters the dangerous concentration range (i.e., time  $\leq 1$  h) suggesting that a potential for an auto-accelerating reaction exists, if the stock flow were to stop. For the ET-grade

caustic soda, the reaction mixture could become dangerous in less than 2 min. At higher temperatures, the reaction conditions become dangerous even more quickly.

When these three triangle diagrams are compared, the importance of impurities (soluble iron) in caustic soda becomes clear. As iron concentration goes up, the reaction contour lines move toward the water apex, suggesting that the danger of explosion covers a wider range of mixture compositions.

#### **Recommendations for safer practice**

While installation costs tend to drive designs of hydrogen peroxide bleaching systems to high concentrations, building systems that are inherently safe is a better choice. By inspection of Figs. 5–7, operating lines can be chosen that do not cross into the regions of dangerous compositions. For example, the dashed pink line in each of the three triangle diagrams (Figs. 5–7) represents the operating line for a mill employing a 10 wt% hydrogen peroxide and 25 wt% caustic soda in the bleach plant. Notice that even a system using ET-grade caustic soda is safe for all compositions. Employee safety is an added benefit of diluting 50% hydrogen peroxide to 10%, before it enters the mill. This lower concentration is less likely to cause permanent damage to skin or eyes.

It was determined that using higher-impurity, iron-containing caustic soda will render the reaction system more dangerous. If a bleaching system employs Hg-cell grade caustic soda, it is possible to safely apply hydrogen peroxide up to 18% without experiencing auto-accelerating decomposition reactions.

Finally, if a peroxide system must be operated with 50% hydrogen peroxide, reliable control systems must be installed to stop the flow of hydrogen peroxide and caustic soda when pulp flow stops. Furthermore, shutdown sequences should

# BLEACHING

include methods for flushing concentrated hydrogen peroxide from collection points like the pumps that exploded [13,14].

## CONCLUSIONS

Hydrogen peroxide decomposition reactions are extremely energy intensive and potentially dangerous. There have been catastrophic events at pulp mills that illustrate the danger. This work evaluated the hydrogen peroxide decomposition kinetics at typical bleach plant concentrations and temperatures. Solutions of all three grades of commercially available caustic soda—ET, membrane, and Hg cell—were employed in these evaluations. Because these three grades of caustic soda differ in their iron levels, the impact of iron-catalyzed decomposition was also quantified. This modeling effort clearly shows that by diluting hydrogen peroxide, an inherently safe bleaching system can be designed, and current bleaching systems should be reevaluated to prevent any further explosions. **TJ**

## ACKNOWLEDGEMENTS

The authors acknowledge the contributions of Brian Brogdon and an anonymous peer reviewer for improving this manuscript with their constructive comments.

## LITERATURE CITED

1. Davies, D., Dietz, T., and Suess, H.U., *Pulp Pap. Can.* 110(8): T142(2009).
2. Parthasarathy, V.R. and Brooks, G., *TAPPI Eng., Pulping Environ. Conf.*, TAPPI PRESS, Atlanta, GA, USA, 2006, Session 18-1.
3. Suess, H.U. (Ed.) in *Pulp Bleaching Today*, Walter de Gruyter, New York, 2010, pp. 201-226.
4. Brogdon, B.N., and Hart, P.W. in *Bleaching of Pulp* (P.W. Hart and A.W. Rudie, Eds.), 5th edn., TAPPI PRESS, Atlanta, GA, USA, 2012, Chap. 10.
5. Hart, P.W. and Rudie, A.W., *TAPPI Eng., Pulping Environ. Conf.* TAPPI PRESS, 2007, Session 9-1.
6. Schumb, W.C., Satterfield, C.N., and Wentworth, R.L., "Hydrogen Peroxide," ACS Monograph No. 128, Reinhold Publishing, New York, 1955, p. 526.
7. Raines, J.C., Schmidt, J.P., Burelach, J.P., et al., *J. Therm. Anal. Calorim.* 85(1):2006(53).
8. Mackenzie, J., *Chem. Eng.* 97(6): 1990(84).
9. Anderson, R., Reid, D., Hart, P., et al., "Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) safe storage and handling -TIP0606-24," Technical Information Paper, TAPPI PRESS, Atlanta, 2010.
10. Solvay Chemicals, "Safety and handling technical data sheet for hydrogen peroxide," Brussels, 2006.
11. Hart, P.W. and Rudie, A.W., *Chem. Eng. Educ.* 45(1): 2011(15).
12. Hoekstra, G., "Explosion rocks mill, two workers injured by blast," *Prince George Citizen*, Prince George, BC, Canada, Feb. 8, 2007.
13. "Ruptured pump may figure into Evadale mill explosion," *Beaumont Enterprise*, Beaumont, TX, USA, Aug. 18, 2001.
14. Stora Enso, *Environmental Statement 2009, Skoghall mill*, Helsinki, Finland, June 28, 2010.
15. Makkonen, H.P. "Decomposition of hydrogen-peroxide in dilute alkaline aqueous solutions," Ph.D. thesis, University of Washington, Seattle, WA, USA, 1971.
16. Galbacs, Z.M. and Csany, L.J., *J. Chem. Soc., Dalton Trans.* 2353(1983).

## ABOUT THE AUTHORS

Feeding 50% peroxide into a pump, which is used as a pulp mixer, can be an inherently hazardous operation. The cause of a mill explosion has been traced to peroxide collecting in a pump when pulp flow was interrupted. We wanted to conduct experiments with hydrogen peroxide and sodium hydroxide using commercial concentrations to better understand the rates of reaction and the nature of the hazard.

Mixtures of hydrogen peroxide and sodium hydroxide can rapidly generate heat and oxygen. We had to exercise great care in designing an experimental system that allowed us to follow the reactions safely. During the course of the study, we realized that the iron contamination of the sodium hydroxide was affecting the rate of reaction. A further difficulty was accurately measuring the iron concentration, which was 0.5–5 ppm, in 50% sodium hydroxide.

As mills either install new or refit existing bleaching systems, they should consider installing a dilution system that will take the peroxide from the stor-



**Hart**



**Houtman**



**Hirth**

age concentration of 50% to 10% before introduction into the mixer. As shown in this study, peroxide at 10% cannot generate an explosive mixture with sodium hydroxide.

*Hart is manager, new technology, MWV Corp., Atlanta, GA, USA. Houtman is a research chemical engineer and Hirth is an analytical chemist, USDA Forest Products Laboratory, Madison, WI, USA. Email Hart peter.hart@mwv.com.*

17. Lapiette, L., Berry, R., and Bouchard, J., *Holzforschung* 57(6): 627(2003).
18. Wuorimaa, A., Jokela, R., and Aksela, R., *Nord. Pulp Pap. Res. J.* 21(4): 2006(435).
19. Popov, E., Väliisaari, J., Vuorenpallo, V-M., et al., *Holzforschung* 61(6): 543(2007).
20. Hart, P.W. and Rudie, A.W., *Pulp Pap. Can.* 111(4): T30(2010).
21. Harris, D.A., *Quantitative Chemical Analysis*, 4th edn., W.H. Freeman, New York, 1995, p. 439.
22. Curlin, L.C. and Bommaraju, T.V. in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edn., Vol. 1. John Wiley & Sons, Hoboken, NJ, USA, 2004, pp. 477–521.
23. Olin Chlor-Alkali Company, "Caustic soda production." Available [Online] at <http://www.olinchloralkali.com/Library/Literature/OverviewOfProcess.aspx>.
24. Skoog, D.A. and West, D.M., *Fundamentals of Analytical Chemistry*, 2nd. Edn., Holt, Rinehart, and Winston, New York, 1969, p. 689.