Understanding the risks and rewards of using 50% vs. 10% strength peroxide in pulp bleach plants

ALAN W. RUDIE AND PETER W. HART

ABSTRACT: The use of 50% concentration and 10% concentration hydrogen peroxide were evaluated for chemical and mechanical pulp bleach plants at storage and at point of use. Several dangerous occurrences have been documented when the supply of 50% peroxide going into the pulping process was not stopped during a process failure. Startup conditions and leaking block valves during maintenance outages have also contributed to explosions. Although hazardous events have occurred, 50% peroxide can be stored safely with proper precautions and engineering controls. For point of use in a chemical bleach plant, it is recommended to dilute the peroxide to 10% prior to application, because risk does not outweigh the benefit. For point of use in a mechanical bleach plant, it is recommended to use 50% peroxide going into a bleach liquor mixing system that includes the other chemicals used to maintain the brightening reaction rate. When 50% peroxide is used, it is critical that proper engineering controls are used to mitigate any risks.

Application: By understanding the risk/reward benefit, chemical pulp mills should realize there is no justification for using 50% peroxide in an extraction stage. If they lower the concentration of peroxide to 10%, their operation will be much safer.

Hydrogen peroxide has been used in the bleaching of both chemical and mechanical pulps for several decades. It is widely recognized as an environmentally friendly bleaching chemical with breakdown products of water and oxygen. Mechanical pulp mills typically use peroxide to obtain higher brightness pulps, with peroxide charges up to 4% on oven dry (o.d.) pulp used in some mills [1,2]. Chemical pulp mills typically employ smaller charges of peroxide (from 0.15%-1.0% on o.d. pulp), often as an oxidative reinforcement in the extraction stage to either reduce the amount of chlorine dioxide required in the first bleaching stage or to raise the brightness of the pulp entering the chlorine dioxide stage that follows [1,3].

Hydrogen peroxide can be and has been used safely for many years, but, like any strong oxidant, it must be handled with caution. Runaway decomposition of hydrogen peroxide has resulted in catastrophic events in pulp mills over the last few years. Several North American chemical pulp bleach plants have experienced catastrophic sudden pressure releases associated with the decomposition of 50 wt% peroxide, resulting in pieces of equipment, such as pump housings, being fragmented and propelled through bleaching towers, building walls, pipes, etc. [4-6]. Although plant personnel were badly injured in at least two of these instances, with the extent of damages, these mills were fortunate to have avoided fatalities in these accidents. Both bleach plants that had personnel injuries experienced a peroxide-induced pressure burst when peroxide and caustic were added to a medium consistency pump in which no pulp was flowing because of undetected operating problems. If pulp had been moving through the process, these explosions would not have occurred, as peroxide would not have been able to pool in the pump or line and decompose in this autocatalytic exothermic reaction. 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 [6-8]. In these cases, the explosion was likely a combination of alkaline-catalyzed decomposition and rapid oxidation of an organic chemical.

Several people have told the authors that other peroxide decomposition incidents have occurred throughout Europe and southeast Asia, but have not been sufficiently documented in the literature to be cited here. Other industries also have experienced problems with rapid peroxide decomposition when using higher concentration applications. For instance, a well-known wine maker using 35% alkaline peroxide to sterilize corks also experienced a rapid decomposition that resulted in an unacceptable work hazard, but there were fortunately no recorded injuries. The Russian submarine Kursh sunk when the 70% peroxide used in the propulsion system of its torpedoes decomposed, with an explosion consequently rupturing the hull [8].

HAZARDS ASSOCIATED WITH THE USE OF HIGH CONCENTRATION PEROXIDE

Hydrogen peroxide is delivered to mills via either tank truck or railcar. Truck deliveries are near 50% concentration [8]. Railcar deliveries may be either at 50% or 70% concentration.
BLEACHING

If a mill receives hydrogen peroxide deliveries at 70% concentration, it is routinely diluted to 50% concentration as it is unloaded into storage. This is done to avoid the rigorous process safety management procedures required for 70% peroxide storage. Under proper storage conditions, hydrogen peroxide decomposes at a rate of about 1% per year [9-14]. Traces of transition metal ions (e.g., iron, copper, and manganese) increase the rate of hydrogen peroxide decomposition [15], and suppliers add stabilizers to sequester these metal ions. Physical contact with 50% concentration hydrogen peroxide solutions poses major safety hazards (e.g., skin burns, eye injuries). It also has the potential for rapid pressurization within tanks, pipes, pumps, and storage vessels. There is a potential for fire due to the formation of oxygen during the highly exothermic decomposition of hydrogen peroxide [9,16]. Despite these potential problems, a 50% peroxide bulk storage tank may be safely managed if proper engineering and administrative controls are employed to prevent contamination and the tank is routinely monitored for temperature rise. Note, however, that two of the serious explosions pulp mills have experienced were storage tanks and directly due to the failure to maintain proper vigilance in handling this chemical.

Chemical pulp bleach plants have routinely handled 50% peroxide without incident, but there is an inherent hazard at this concentration that makes it difficult to eliminate all risks of explosions and fires. If one accepts the “what can go wrong will go wrong” philosophy and that operations managers must eliminate risks to personnel and facilities from a worst-case scenario, it is hard to justify use of the chemical at 50% strength. Startup or shutdown failures, pump failures, blocked lines, or ruptured pipes or seals that could result in a small pool of 50% peroxide present potentially catastrophic conditions. Even when diluted to 10% strength, there is potential for personal injury from leaking pumps and piping. Although it cannot completely eliminate the risk of injuries, dilution of 50% peroxide to 10% significantly reduces the reaction rate, providing critical time to address exposure in the event of a spray from a leaking gasket or seal [9], and this will usually decrease the severity of injuries significantly.

Storage tank hazards
A common hazard associated with 50% peroxide solutions is vessel rupture caused by peroxide decomposition. Vessel rupture occurs when the gas generation rate exceeds the venting capacity of the storage tank [9]. Catalytic decomposition of peroxide results in the liberation of oxygen and heat. One liter of 50% hydrogen peroxide can yield approximately 200 L of oxygen, in addition to steam. Under typical circumstances, hydrogen peroxide is stored at 50% concentration. This provides sufficient water to absorb any heat evolved due to normal slow (unaccelerated) peroxide disproportionation. The thermal mass also provides time to take actions to prevent catastrophic outcomes if the tank becomes contaminated and decomposition accelerates. In high concentrations, a catalytic decomposition can become self-accelerating because the rate of heat evolution exceeds the rate of heat loss to the surroundings [10]. Vaporization of water results in further concentration of the hydrogen peroxide solution, which results in faster decomposition. Vessel ruptures have occurred in both Europe and North America when an organic chelant was mistakenly unloaded into hydrogen peroxide storage tanks [6-8]. In these cases, the explosion was likely a combination of alkaline-catalyzed decomposition and rapid oxidation of an organic chemical.

Hydrogen peroxide is typically stored at around 50% concentration in a mill. If it is shipped into the mill site via rail, it is possible to have it arrive at the mill at a higher concentration. The peroxide is diluted to about 50% at the point of unloading as it is being sent to storage. Mills generally store peroxide at 50% concentration to reduce capital costs, as considerably larger storage tanks would be needed to store peroxide at lower concentrations. Also, by storing at 50% concentration, the mill does not have to designate the storage tank and associated process piping as a process safety management (PSM) covered process. Fifty percent peroxide can be stored safely with proper precautions and engineering controls. Hydrogen peroxide storage tank temperature should be monitored. The decomposition process is typically slow at first and may take days or weeks to become “critical”. A temperature increase of Δ1°C per hour, at 30°C–35°C, is indicative of a decomposition event. Decomposition reactions in storage can be quenched by external cooling or dilution.

Pressure burst hazards
Another failure mode for alkaline peroxide is a pressure burst occurring within processing equipment. At least two mill explosions have resulted from pressure bursts within the last several years [9]. Extensive kinetic modeling has been performed to predict pressure bursts from first principles models [10,11]. The initial modeling work used kinetic data for dilute peroxide developed by Makkonen [12] under laboratory conditions. A limitation of this work was that process model kinetics were extrapolated well beyond the experimental range of temperatures and concentrations from which the model was developed. Such large extrapolations have the potential to introduce substantial errors into the model predictions. To improve the kinetic modeling, additional experiments were conducted with chemicals, concentrations, and temperatures similar to bleach plant operating or startup conditions, and these results were used to reduce the extrapolation error [13].

DISCUSSION
The kinetics of decomposition were experimentally measured for mixtures of hydrogen peroxide and sodium hydroxide based on commercial diaphragm grade, membrane grade, and mercury cell grade sodium hydroxide and commercially available 50% hydrogen peroxide [13]. These results were used in a model to develop the three-component triangle diagram shown in Fig. 1. Decomposition rates when using membrane grade caustic were used to develop this diagram. The contour
1. 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 with 50% peroxide. The pink line is the proposed safer operating line when 12% peroxide is employed.

Lines in the triangle diagram represent the time required for the reaction mixture to reach 100°C and enter a potentially explosive condition. Typical high concentration bleaching chemicals are 25 wt% caustic and 50 wt% peroxide. All mixtures of 25 wt% caustic soda and 50 wt% hydrogen peroxide will be somewhere on the thick line on the triangle diagram. This line represents the operating line when there is no pulp flowing in the system. Notably, the operating line enters the dangerous concentration range (arbitrarily chosen as 1 h), which suggests that an auto-accelerating reaction could occur in a mill using 50% peroxide if the stock flow that dilutes the chemicals were to be interrupted. Inspection of Fig. 1 shows that there is a region of inherent safety using hydrogen peroxide with a concentration below 12% (see the dotted fuchsia colored line representing 12% peroxide and 25% caustic). In order to account for process control fluctuations and provide a small safety factor, the authors are suggesting 10% concentration as the “relatively safe” concentration of peroxide for bleach plant application.

Startup condition modeling for chemical and mechanical pulps

The alkali catalyzed peroxyde decomposition reaction occurs when caustic is mixed with peroxide. This is a parasitic reaction that is always present in pulp bleaching but is typically a minor loss of reagent when bleaching proceeds normally. Without pulp present, alkaline catalyzed decomposition will consume the peroxide and generate considerable heat in the process. Catastrophic events appear to require a partially contained pool or supply of peroxide that can maintain the reaction long enough for the temperature and reaction rate to rise beyond the vent capacity of the system to release the steam and oxygen gas. Typically, this scenario—a pre-existing pool of peroxide—only occurs during non-standard operating conditions such as shutdowns, startups, or equipment failures.

Modeling was used to evaluate typical startup scenarios for both chemical and mechanical pulp bleaching processes. Chemical pulp mills usually employ direct injection of peroxide and caustic into a flowing pulp stream at the inlet of a pump; evaluation of this mixing system showed that one particular failure mode leads to an incredibly unstable situation. If caustic is added to a pre-existing pool of high concentration (50%) hydrogen peroxide—the autocatalytic reaction—can exceed the vent capacity of typical mixers and pumps causing the pressure to rise above atmospheric pressure. The kinetic model shows this as a runaway condition, and the predicted pressure buildup is quite sudden, very substantial and can exceed the ability of piping and pumps to contain the reaction. This model mimics at least one of the known explosions exceptionally well. When 10% peroxide is used, the water absorbs all the heat that is generated by the decomposition, and without the steam generation, the reaction does not build as much pressure and does not exceed the large vents of the suction and discharge of pumps or mixers [10,11,13].

High consistency peroxyd bleaching in mechanical pulp mills has been used for nearly five decades. The key process
BLEACHING

2. Addition of hydrogen peroxide prior to the bleach liquor tank [9]. Water and caustic, sometimes with Epsom salts, are combined. The resulting solution is blended with silicate. Peroxide is added to this stabilizing mixture and either sent to a day tank or pumped directly into the pulp being bleached.

3. In-line dilution of the hydrogen peroxide bleach liquor [9].

4. Typical dilution system to supply 10% peroxide from a 50% storage tank to a chemical pulp bleach tower

Hydrogen peroxide is typically added to the bleach liquor flow, which provides a redundant control process so pools of undiluted peroxide should not accumulate within the process. As a comparison, a typical peroxide dilution system used to bring peroxide from nominally 50% concentration to about 10% concentration for chemical pulp bleaching systems is shown in Fig. 4.

For the startup scenarios evaluated for the cascade type mixing systems used to prepare mechanical pulp bleaching solutions, failure of one part of the mixing process or supply system is predicted by the kinetic model to result in stable solutions or slow decomposition rates that can be readily managed even when 50% peroxide is being mixed with the other chemicals used in the bleaching system. Even when water flow fails, models of the addition of 50% peroxide to sodium hydroxide do not predict a significant pressure rise, partially because the gas is released in a steady stream as peroxide is added.

DIFFERENCES BETWEEN MECHANICAL AND CHEMICAL PEROXIDE BLEACHING

One of the main driving forces of medium consistency (MC) chemical pulp bleaching is the current ability to mix chemicals into pulp at 10%–15% pulp consistency. This is a desirable outcome of improved mixing technology because several bleaching chemicals, including hydrogen peroxide, have faster reaction rates at higher solution concentrations. One of the main tenets of MC bleaching is to keep as much water as possible out of the bleach plant by using stronger bleaching chemicals. Hence, some bleach plant suppliers now quote 50% peroxide as the required strength for their bleaching systems. Typical operating scenarios for both chemical pulp mills operating at MC conditions and mechanical pulp bleach plants operating at higher consistency have been evaluated to determine the impact of peroxide strength on the initial bleach tower peroxide concentration.

There are fundamental differences in peroxide bleaching for mechanical pulps and chemical pulps. Peroxide has limited effectiveness as a bleaching agent when used as an oxida-
positive reinforcement of the extraction stage in chemical pulp bleaching and tends to be limited to about 1 wt% charge on o.d. pulp or less. Since most trace transition metal ions are removed in the first bleaching stage, peroxide stabilization is not typically a problem. When peroxide stabilization is required, it is usually accomplished with a chelating chemical (EDTA or DTPA) and sometimes with magnesium sulfate (Epsom salt). An increase in the concentration of the peroxide feed affects the concentration of the peroxide in the pulp, as shown in Fig. 5, as a function of the starting pulp consistency for a 1% peroxide charge on pulp. Note that peroxide concentration in the bleach tower is directly related to the reaction rate, and higher peroxide concentrations are best achieved with higher pulp consistency.

As is readily seen, at 1% charge on pulp, there is almost no increase in the solution concentration of peroxide during bleaching due to increases in peroxide concentration, even at very high peroxide concentrations of 50%. In comparison, raising pulp consistency before mixing is far more effective at increasing the peroxide concentration and reaction rates, but typical chemical pulp processing with MC pumps and towers limit the pulp consistency to 20% or less. At 20% pulp consistency before mixing, the impact of the as-delivered peroxide concentration is negligible, 0.072 moles/Kg for 50% strength peroxide compared to 0.071 moles/Kg at 10% peroxide strength. That represents about a 1.5% increase in solution concentration and reaction rate when using 50% peroxide compared to 10% peroxide. The safety concerns associated with the use of 50% peroxide far outweigh the value of the minimal enhancement in peroxide efficiency resulting from the use of 50% peroxide.

Peroxide stabilization is a challenge with mechanical pulps, which contain significant trace levels of manganese and iron. Stabilization usually starts with addition of a chelating chemical, followed by pressing to remove as much of the trace transition metal ions as possible; pressing results in a
bleaching

pulp consistency of 25%-35%. A peroxide cocktail or bleach liquor that contains sodium silicate, magnesium sulfate, sodium hydroxide, and peroxide is then mixed with the pulp. The combination of chemicals required to stabilize the peroxide makes the use of peroxide for bleaching mechanical pulps more expensive. A typical peroxide charge under these conditions is 3 wt% or 4 wt% on o.d. pulp. The impacts of both the starting pulp consistency and peroxide strength when using a 4% peroxide charge on pulp are shown in Fig. 6.

As seen previously with the chemical pulp bleaching scenario, the starting pulp consistency in mechanical pulp bleaching has the larger impact on the peroxide concentration, relative to peroxide reagent concentration; hence, pulp consistency has the larger impact upon the peroxide bleaching reaction rate. At the high peroxide charge and high pulp consistency, the peroxide concentration can offer a marginal increase in concentration (and thus reaction rate). At 40% consistency for the pressed pulp (about the maximum that can be achieved with a twin wire press), the 10% peroxide strength provides a solution concentration of 0.606 moles/Kg, while the 50% peroxide solution increases this to 0.726 moles/Kg. Therefore, using 50% peroxide solution will result in about a 20% increase in reaction rate versus using a 10% strength peroxide solution.

**CONCLUSIONS**

An evaluation of the advantages and risks associated with storage and point of application of high versus low concentration hydrogen peroxide was performed. The major safety problems related to concentrated hydrogen peroxide use are the potential for rapid pressurization from catalyzed decomposition, fire due to oxygen formed in decomposition, and peroxide/organic vapor phase explosions. As peroxide is a strong oxidizing agent, 50% peroxide can cause severe burns when it contacts skin. Lowering the concentration of peroxide in storage will result in excessively sized storage tanks resulting in substantial increases in capital costs. Table I lists a series of recommendations for safer practices that balance capital costs, personnel and equipment risks, and bleaching performance.

Fundamental differences exist between mechanical pulp bleaching with peroxide and chemical pulp bleaching with peroxide. In general, mechanical pulp bleaching uses considerably higher charges of peroxide on o.d. pulp than chemical pulps and often uses higher consistencies than can be obtained with traditional chemical pulp washers, pumps, and mixers. The current work quantifies the benefit of using 50% peroxide in both bleaching processes compared to 10% peroxide. This work also reviewed the safety hazards associated with peroxide and how they differ for storage strength 50% versus diluted-strength 10% concentrations. In general, the use of 50% peroxide in mechanical pulp bleach liquors is considerably safer and provides a larger benefit than the use of 50% peroxide in chemical pulp mills.

For chemical pulp bleach plants, the benefit of operating with 50% peroxide instead of using the inherently safer 10% peroxide solution is very marginal. The boost in the reaction rate from the higher concentration is estimated at just 1.5%.

<table>
<thead>
<tr>
<th>Process</th>
<th>Recommendation</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Storage Tank</strong></td>
<td>Store at about 50% concentration</td>
<td>Capital cost is too high vs. minimal risk as long as good controls are in place and followed</td>
</tr>
<tr>
<td></td>
<td>Engineering controls – Temperature monitoring</td>
<td>Early warning of decomposition with enough lead time to mitigate issues</td>
</tr>
<tr>
<td></td>
<td>Engineering Controls – Vents</td>
<td>Allow slow decomposition products to escape tank instead of gradually building pressure</td>
</tr>
<tr>
<td></td>
<td>Administrative Controls – Unloading protocols</td>
<td>Signoff procedure as last line of defense from allowing wrong material to be unloaded into peroxide tank</td>
</tr>
<tr>
<td><strong>Mechanical Pulp Bleaching</strong></td>
<td>Use a mechanical device to make down a stabilized bleach liquor</td>
<td>Prevents rapid decomposition by stabilizing peroxide and dilutes high concentration peroxide to considerably lower concentrations</td>
</tr>
<tr>
<td></td>
<td>Use 50% peroxide to free bleach liquor makedown system</td>
<td>Improves bleaching reaction by about 20% compared to using 10% peroxide. Bleach liquor is substantially diluted and stabilized prior to entering the pulp stream</td>
</tr>
<tr>
<td><strong>Chemical Pulp Bleaching</strong></td>
<td>Use 10% concentration peroxide</td>
<td>Very limited kinetic benefit as compared to using 50% peroxide. Enough water is present to prevent explosive decomposition reactions from occurring</td>
</tr>
</tbody>
</table>

*1. Suggested conditions for balanced operation.*
For mechanical pulp bleaching at 40% pulp consistency and 4% applied peroxide on pulp, the use of 50% peroxide resulted in about a 20% increase in reaction rate compared to the use of 10% peroxide. Mechanical pulp mills do not have the history of peroxide-based explosions that have occurred in chemical pulp peroxide bleach plants. This is due to a combination of differences in the processes: the use of a cocktail of chemicals needed to stabilize peroxide in mechanical pulp bleaching provides dilution and stabilization, and the use of high consistency refiner-like mixers that do not provide volume where a pool of peroxide is able to collect in during a process upset.

**LITERATURE CITED**


**ABOUT THE AUTHORS**

Vendors have been promoting the use of 50% peroxide in medium consistency (MC) bleach plants for many years due to the increase in reaction rate associated with higher concentration chemicals. It has been well documented that risk potential increases as the concentration of certain chemicals is increased. We decided to see what the actual risk/reward proposition was to determine if the use of 50% peroxide was truly justified.

Past research has looked at modeling the peroxide reaction and determining the conditions that result in an explosion. The impact of various industrial chemicals and operating conditions was also evaluated. This is the first study that determined the benefits of using the higher concentration peroxide and compared it with the associated elevated risk.

Deciding how to treat the differences between chemical and mechanical pulp bleaching was the most difficult aspect of this research. We reviewed and modified our approach a couple of times to make the paper concise and still convey the differences.

The impact of pulp consistency was surprising. Increasing the pulp consistency far overwhelmed the impact of chemical concentration.

By understanding the risk/reward benefit, chemical pulp mills should realize there is no justification for using 50% peroxide in an extraction stage. If they lower the concentration of peroxide to 10%, their operation will be much safer.

We have modeled the decomposition reaction using both ideal and industrial conditions. We also determined areas of safer operating conditions and described the differences between chemical and mechanical bleaching conditions. With this work, we developed the risk/reward associated with using 50% vs. 10% peroxide and have basically completely this line of research.

Rudie is assistant director, U.S. Department of Agriculture Forest Products Laboratory, Madison, WI, USA. Hart is director, Fiber Technology and Innovation, at WestRock, Richmond, VA, USA. Email Hart at peter.hart@westrock.com.