A Comparative Evaluation of Explosion Hazards in Chemical and Mechanical Pulp Bleaching Systems

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ABSTRACT
Over the past several years, at least three pulp mills in North America have experienced catastrophic events that resulted in the explosion of pumps, mixers, and tanks. All these mills were using 50% concentration hydrogen peroxide at the site of the explosions. In at least two instances, alkalicatalyzed decomposition of peroxide is implicated in the explosion. Although many mechanical pulping facilities use hydrogen peroxide to bleach pulp, no alkali–catalyzed explosions have been reported. The current work uses a kinetic model of peroxide decomposition to explain why the peroxide bleaching process typically used for mechanical pulps has lower risks than some of the processes used to bleach chemical pulps. Safe mechanical pulp bleach liquor preparation practices are also discussed.

KEYWORDS
Hydrogen peroxide decomposition, kinetic model, mechanical pulp bleaching, caustic

INTRODUCTION

Hydrogen peroxide is a well-known bleaching agent in both chemical and mechanical pulp mill bleach plants. It can be and has been used safely for many years, but like any strong oxidant, it must be handled with respect. The major safety problems related to 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. Within the past 15 years, at least three chemical pulp bleach plants in North America experienced catastrophic equipment failures associated with the use of 50 wt% peroxide [1,2]. People were badly injured in two of these instances, and these two mills were fortunate to have avoided fatalities in these events. Both bleach plants experienced a peroxide-induced pressure burst when peroxide and caustic were added to a mediumconsistency pump and pulp flow did not start due to operating problems. The thud incident was a contamination case that occurred at the Uniforêt mill in Port Cartier, Quebec, in 1993 [3].

Several significant differences in chemical and mechanical pulps have led to very different bleaching processes. Mechanical pulps typically contain high enough concentration of manganese and iron to decompose a significant portion of the peroxide used in bleaching pulp [4]. To minimize decomposition, mechanical pulp mills usually use a bleaching solution containing sodium silicate and magnesium sulfate as peroxide stabilizers. In comparison, most trace metals are removed in the first stage of bleaching for chemical pulps, and addition of peroxide stabilizers is usually not necessary.

Mechanical pulps use peroxide as the primary bleaching agents and typically require 1% to 3% charge on pulp. In comparison, peroxide is a supporting delignification reagent in most chemical pulp bleach plants and is used at less than 0.5% on pulp. The high chemical charge in the case of mechanical pulps justifies more capital and the result is a stage optimized for peroxide bleaching: a press to enable bleaching at 20% consistency and a specialized mixer to mix chemicals efficiently in the absence of free water. The low charge of peroxide in most chemical bleaching systems does not justify significant capital expense, and

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these stages are usually very similar to other chemical bleaching stages such as chlorine dioxide and caustic extraction.

The high consistency used in bleaching mechanical pulp benefits the process in two ways. Mechanical pulps are low drainage pulps and generally have had very little washing that could remove trace metals before peroxide bleaching. Pressing the pulp from 3% to over 20% consistency removes as much as 88% of the soluble metals, providing significant benefit in peroxide stability and bleaching efficiency. For a case using 3% peroxide on pulp at 20% consistency, the initial peroxide concentration is over 0.2 M, more than twice the concentration and consequently more than twice the reaction rate obtainable at a more conventional 10% consistency. This also provides a noticeable improvement in the performance of the bleaching stage. For chemical pulps, the preceding stage washer discharges at 12% to 14% consistency and chemicals are added either by simultaneous injection into a medium-consistency pump or mixer or by mixing caustic in the repulper of the preceding stage and adding peroxide at the mixer. The two different systems have resulted in different standard practices in supplying peroxide to the pulp mixer. The additional chemicals and the need to provide sufficient volume to obtain uniform chemical distribution in the high-consistency mixer necessitate considerable dilution for mixing peroxide with mechanical pulps and the resulting solution is typically about 10% peroxide. Chemical pulp mills have few requirements, and this has resulted in a lack of standardization for handling peroxide. Without installing the specialized equipment used in mechanical pulp bleaching, the only way to increase the peroxide concentration in a chemical mill is to start at a higher peroxide solution strength. Some mills or suppliers have taken this approach, supplying 50% peroxide direct from storage to the pulp mixer. Most have elected to dilute to 10% strength for distribution in the mills. Although the approach is sound in theory, in practice the higher peroxide strength appears to have little benefit– Assuming the washer is discharging at 14% consistency and the peroxide charge is 0.5% on pulp, the final peroxide stage consistency and peroxide concentration are 13.9% and 0.0237 M when peroxide is added as a 10% solution, and 13.98% and 0.0239 M when it is added using a 50% solution. This is not a large enough difference to have a noticable impact on stage efficacy.

In an effort to understand the hazards associated with hydrogen peroxide use in both chemical and mechanical pulp bleaching systems, the current work employs a dynamic kinetic model of caustic-induced hydrogen peroxide decomposition to determine conditions that lead to potentially explosive situations. The hazardous conditions identified are then examined relative to typical procedures for bleach liquor preparation and addition in both mechanical and chemical pulp bleaching systems. The potential hazards for each type of system can then be evaluated.

PEXROXIDE DECOMPOSITION

Gas generation, volumetric expansion

In general, peroxide is a stable chemical, decomposing slowly at a rate less than 1% per year [5]. If mishandled, peroxide can decompose rapidly and becomes a serious chemical hazard. The most serious peroxide accidents usually involve one of three types of decomposition processes:

- decomposition resulting from organic contamination,
- decomposition resulting from inorganic contamination, or
- decomposition under alkaline conditions.

The peroxide reaction with organic materials is an oxidation reaction much like combustion. The decomposition reactions from inorganic contamination and base catalysis are similar. These are a disproportionation reaction recombining two moles of peroxide to produce a mole of oxygen and two moles of water [6,7]:

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O + O_2 \qquad \Delta H = -14.3\ \text{kcal/g-mol} \qquad [1]$$

The reaction is highly exothermic and the temperature rise from decomposition increases the rate of decomposition—a critical condition for a runaway reaction.

Using the heat of reaction [7] and ideal gas law, the adiabatic volumetric expansion can be calculated for hydrogen peroxide at various strengths (Figure 1) [3,8]. Between the 1.5 mol of gas evolved from the

decomposition and the water vapor produced from the heat of reaction, extremely large volumes of gas can be produced at the higher peroxide concentrations. The water produced by the decomposition remains liquid until the temperature reaches 100°C. At about 10% peroxide concentration, the heat from peroxide decomposition is sufficient to raise the solution from room temperature to 100°C, and the decomposition begins to generate steam. At about 60% concentration, insufficient water is available to carry away the heat of reaction as steam, and the gas temperature rises above 100°C, causing additional thermal expansion. Use of dilute solutions provides an inherent risk reduction although it cannot remove all risk.

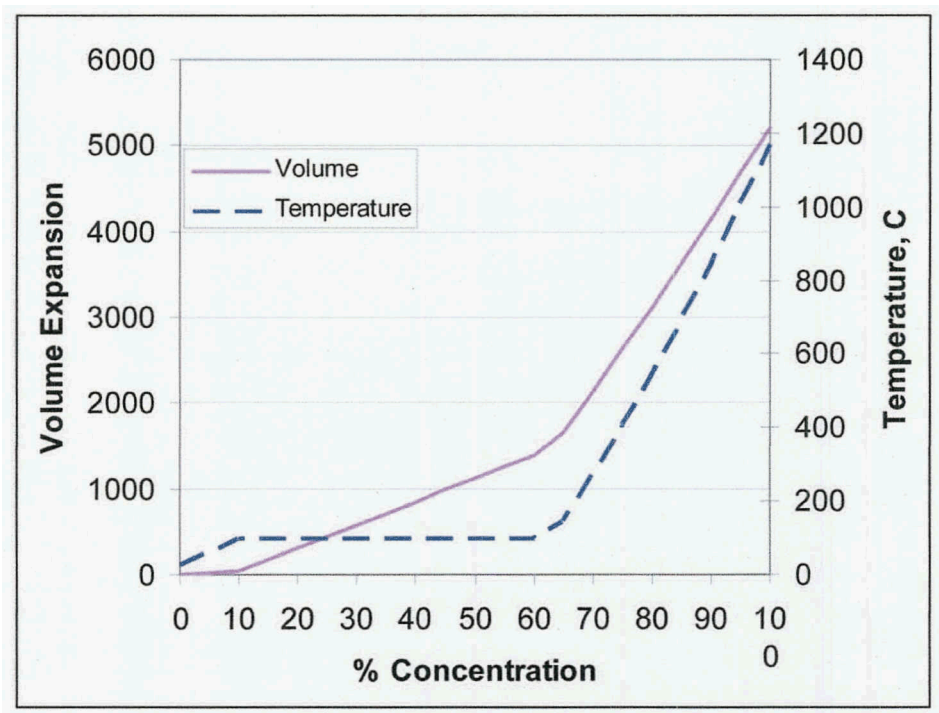

Figure 1. Temperature and adiabatic volume of oxygen and steam resulting from the decomposition of a single volume of hydrogen peroxide solution. Volumetric expansion is liters of gas produced per liter of peroxide solution.

Alkali-Catalyzed Peroxide Decomposition Kinetics

Alkali-catalyzed decomposition of hydrogen peroxide follows second-order reaction kinetics as shown in equation 2 [7]. The rate of decomposition depends on both the acid (HOOH) and base (HOO^-) forms of peroxide:

$$dP/dt = -k[HOO^-][HOOH]$$

where P is total peroxide concentration (both acid and base forms) and t is time.

The apparent rate constant reported by Makkonen is 8×10^{-3} L/mol/s at 45°C [7]. The apparent rates follow the Arrhenius theory within the temperature range of Makkonen's experiments, giving an activation energy of 13.1 kcal/mol [7]. The rate is reported as an apparent rate since it is condition dependent and the decomposition from alkaline catalysis cannot be completely separated from decomposition due to trace transition metals, which is also pH dependant [9]. As examples, Makkonen measured slower decomposition for reactions stabilized with magnesium or silicate [7], and Galbacs and Csanyi reported rates as low as 10^{-6} L/mol/s using extreme efforts to minimize inorganic contamination [9]. Because mill conditions are invariably heavily contaminated, the Makkonen kinetic measurements provide a conservative estimate of the apparent decomposition rate and a convenient basis for developing a dynamic kinetic model.

Dynamic Kinetic Modeling

To evaluate conditions that could lead to catastrophic peroxide decomposition, a kinetic model was prepared in an Excel spreadsheet (Microsoft Corp., Redmond, Washington) integrating the reaction kinetics using Euler's method. Details of the model were published elsewhere [3, 8]. The model can vary peroxide and caustic concentration and evaluate pressure build-up for closed systems or situations with some gas escape, as would occur in a pump or mixer.

Several design configurations were evaluated using the kinetic model developed earlier. Early scenarios had included adiabatic conditions and gas-vented conditions. For the vented cases, gas flow was estimated using the square root relationship between mass flow and differential pressure [10] and assuming a 10-cm-diameter orifice.

$$M/\mathrm{s} = 0.0252\sqrt{\frac{(P_\mathrm{h} - 10100)P_\mathrm{h}}{T}} \qquad [3]$$

where M is mass, P_h pressure at the high-pressure side of the orifice, and T temperature in kelvins.

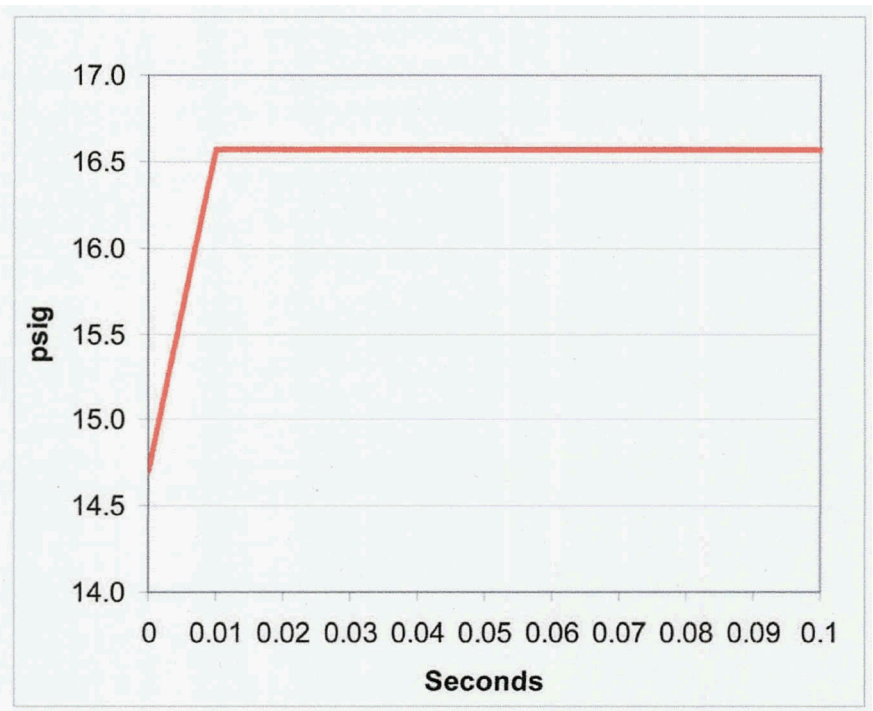

Figure 2. Pressure change when 50% peroxide is added to the CSTR-type mixing chanber containing 3.25 gallons of 25% caustic-first 1/10 s. Note that reaction pressure has stabilized at the first time increment.

All dynamic scenarios for evaluating mill mixing systems in this paper used the 10-cm-diameter vented model. The model involves a number of approximations. First among these is the orifice constant, which is typicallly around 0.85. The model also assumes no significant rate acceleration from equipment surfaces or contaminants and estimates kinetic rate at temperatures well beyond the range evaluated by Makkonen [7]. The errors in these assumptions can be substantial. Additionally, the presence of sodium silicate and/or chelant reduces the reaction rate. Because the purpose was to evaluate worst-case-scenarios, these mitigating factors were not considered. The value of the model is in demonstrtating features of the porcess that can predispose the process to catastrophic decompositons but not in identifying condtions that are

certifiably safe. The model is also capable of determining the impact of order of chemical addition and change m concentration of the acid and base forms of peroxide as the decomposition reaction progresses. The model was used previously to identify specific system failures that contributed to the runaway reactions experienced by the two chemical pulp mills [3].

Scenario 1: Simultaneous mixing of 50% peroxide and 25% sodium hydroxide

The first scenario examined the decomposition for a startup condition mixing diluted caustic with 50% hydrogen peroxide. As shown in Figure 2, the peroxide caustic solution rapidly reaches a decomposition equilibrium condition that results in a very slight pressure rise easily contained within the system. Maintaining flow rates simply results in a steady increase in the base form of the peroxide (HOO^-), and the low residual concentration of acid form controls overall rate and causes the reaction to become self-limiting. Figure 3 shows the gradual build-up of the base form of hydrogen peroxide over the first 100 s of adding peroxide to the mixing tank. The acid form ofperoxide remains below 0.01 M.

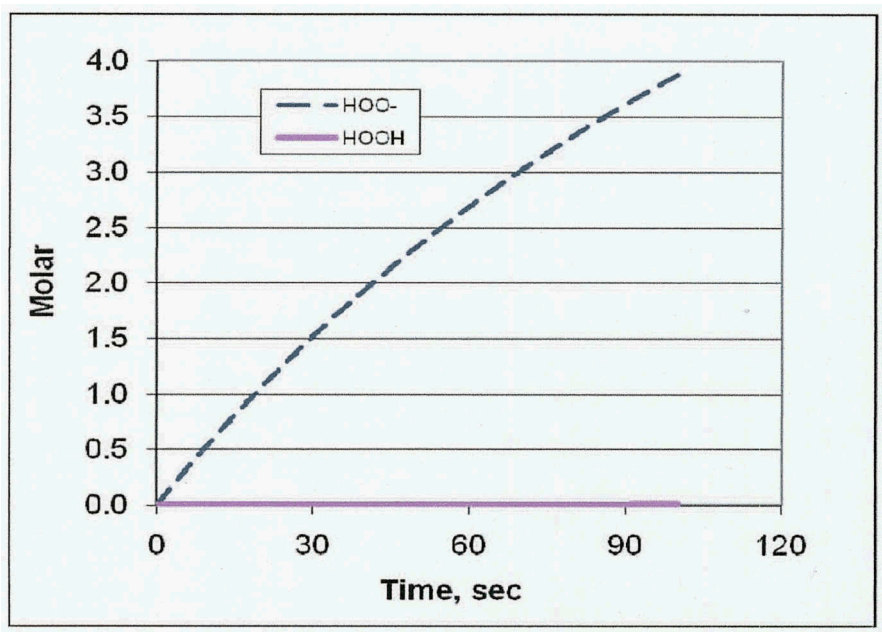

Figure 3. Concentration of acid and base forms of peroxide for the first 100 s. There is never sufficient acid form to accelerate the reaction.

Scenario 2: Delayed addition of Sodium Hydroxide

When caustic is added to a preexisting pool of high concentration (50%) hydrogen peroxide, the pressure rise is quite sudden and very substantial. (Figure 4) This reaction scenario is no longer self-limiting. Instead of a steady or declining rate dictated by the limited concentration of the acid form of peroxide, as the caustic increases, the reactant ratios approach ideal. Temperature and kinetic rise, causing an acceleration of the reaction rate and much higher gas and steam pressures. Because the reaction rate does not begin to slow until the acid form of the peroxide is nearly exhausted, the ultimate rate, temperature, and pressure are limited principally by the initial concentration and volume of peroxide (Figure 5). This scenario mimics the conditions thought to have preceded at least one of the two catastrophic mill incidents.

Other Scenario's Examined:

Several other systems were evaluated. All scenarios using dilute peroxide (10% or less) fail to produce the unmanageable pressure spikes observed in the second scenario (Figure 4). This is primarily because there is sufficient water to prevent boiling, and well-designed peroxide storage systems provide sufficient vent area to prevent a significant pressure build up. Low peroxide strength therefore provides an inherent improvement in safety to peroxide mixing systems. Unvented vessels and pipe supply systems can still

encounter substantial pressures. A scenario with delayed peroxide addition provided an outcome similar to that of scenario 1. When the hydrogen peroxide starts to enter the reaction system, it rapidly converts to the base form. Because the alkali is not consumed in the reaction, any increase in the kinetic rate of decomposition quickly consumes the residual acid form peroxide, which becomes the limiting reagent that controls reaction rate.

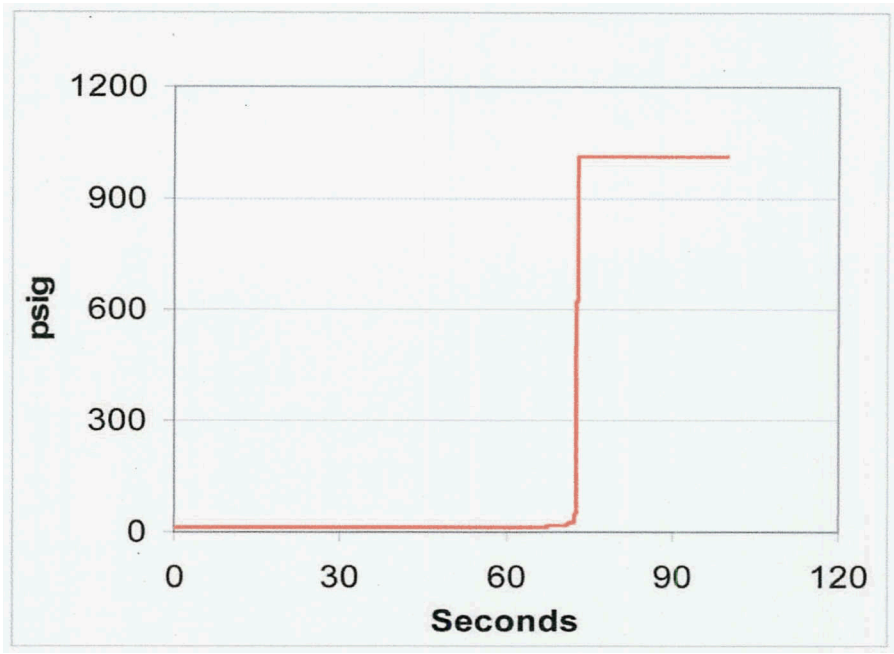

Figure 4. Estimated pressure for a scenario using 50% peroxide and 35% sodium hydroxide. The vented mixing vessel contained 25 L of peroxide prior to alkali addition.

CONCLUSIONS

The general arrangement of typical mechanical pulp bleaching liquor preparation systems makes them relatively safe to operate. Concentrated hydrogen peroxide is added into a flowing or mixed stream of diluted caustic. The presence of sodium silicate, magnesium sulfate, and/or chelant help to slow the decomposition reaction, and the dilution water reduces concentrations and adds a large thermal mass that absorbs the heat from decomposition that does occur. Once the peroxide concentration is below 10 wt%, the potential for catastrophic pressure rises is substantially reduced although not completely eliminated.

Chemical pulp bleaching systems do not always have this designed-in safety. Some systems use caustic and peroxide as received or stored, resulting in very high concentration mixing. These mills can generally operate safely, but under upset condition where the pulp flow is interrupted and caustic flow starts late, the pool of high concentration peroxide can decompose at accelerating rates and overload the vent capability of the system and in worst case scenarios, the pressure handling capability of the equipment. The reason this scenario results in a significant pressure spike is that the reservoir of peroxide continues to feed the reaction while temperature and kinetic rate increase. By contrast, there is no reservoir of reactive peroxide when the caustic is diluted in the mixing tank and used as dilution for peroxide being added into an exit stream of a cascade mixer or series of static mixers.

The dynamic kinetic model of alkali-catalyzed peroxide decomposition used in this evaluation appears to mimic mill experience nicely. It has identified one specific set of conditions that should result in significant pressure spikes and potentially catastrophic consequences. This scenario appears to match the conditions

thought to have preceded one of the two catastrophic failures that have been recorded in chemical pulp bleaching systems. Although eliminating all hazards in working with energetic chemicals is impossible, experience and the kinetic model both suggest that the risk of catastrophic pressure spikes can be greatly reduced by diluting the peroxide to 10% strength for distribution to the bleach plant.

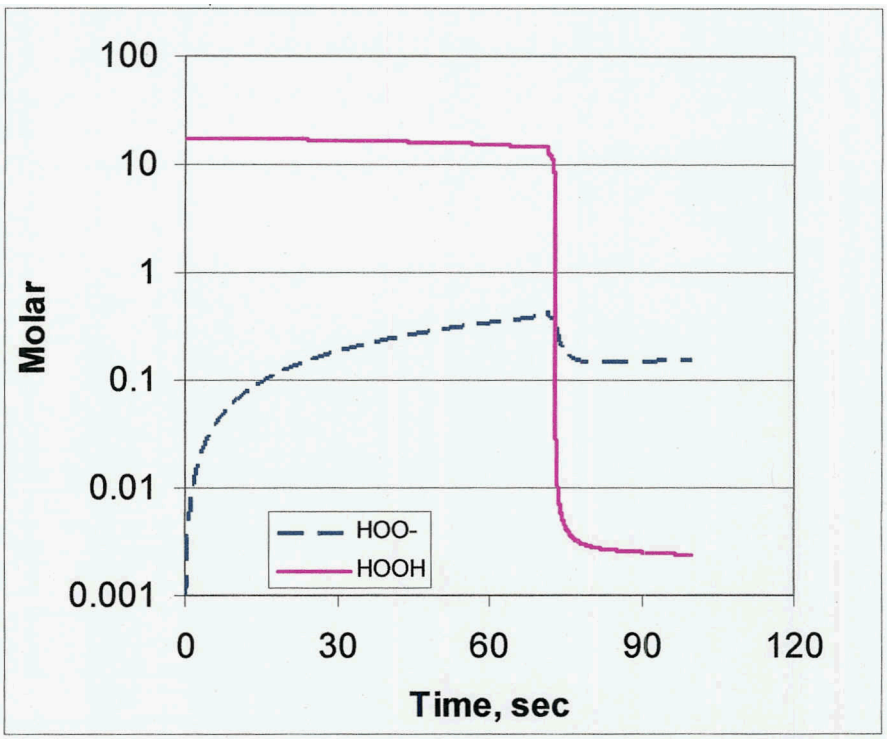

Figure 5. Concentrations of H_2O_2 and HO_2 as estimated by the kinetic model for the situation in Figure 4.

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