The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. We request problems that can be used to motivate student learning by presenting a particular principle in a new light, can be assigned as novel home problems, are suited for a collaborative learning environment, or demonstrate a cutting-edge application or principle. Manuscripts should not exceed 14 double-spaced pages and should be accompanied by the originals of any figures or photographs. Please submit them to Dr. Daina Briedis (e-mail: briedis@egr.msu.edu), Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824-1226.

MODELING AN EXPLOSION: THE DEVIL IS IN THE DETAILS

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The Chemical Safety and Hazards Investigation Board has recently encouraged chemical engineering faculty to address student knowledge about reactive hazards in their curricula. This paper presents a simple approach that may be used to illustrate the importance of these types of safety considerations.

The use of hydrogen peroxide in pulp bleaching has increased considerably over the past decade. It has been promoted as an environmentally friendly chemical because the final decomposition products are oxygen and water. Peroxide is easy to use and has found industrial applications ranging from nuclear plant decontamination[1] to waste-water treatment.[2] Hydrogen peroxide is not even covered by Process Safety Management (PSM) regulations in concentrations under 53 wt% and in quantities less than 7,500 lb (3,410 kg).[3] As such, many people assume that hydrogen peroxide is inherently safe. Quite the contrary, at the higher concentrations used in industry, hydrogen peroxide can be extremely dangerous. The sinking of the Russian submarine Kursk[4] was attributed to an explosion caused by high-concentration peroxide leaking from a damaged torpedo. Explosions in receiving tanks[2, 5] and paper industry bleach plants[6, 7] are evidence to the potential energy and hazards incumbent in using 50% hydrogen peroxide.

The major safety problems related to hydrogen peroxide are skin burns and eye injuries from direct contact, the potential for rapid pressurization, the potential for fire due to oxygen formed in decomposition, and peroxide-organic vapor phase explosions. Over the past 15 years, at least three bleach plants in North America experienced catastrophic events involving the decomposition of hydrogen peroxide.[6, 7, 9] Pumps exploded in two of these events, each resulting in serious injuries. Both mills were using 50 wt% peroxide and had been using it without incident for several years. Both bleach plants experienced a peroxide-induced pressure burst when

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peroxide and caustic were added to a medium-consistency pump, and pulp flow did not start due to operating problems. The third incident was a contamination case that occurred at the Uniforêt mill in Port Cartier, Quebec, in 1993.[9]

Of very recent importance to chemical engineers is the explosion at the T2 Laboratories in Jacksonville, Fla. On Dec.19, 2007, the T2 Laboratories lost cooling control of a reaction between sodium metal and cyclopentadiene, resulting in a massive explosion and four fatalities. In their report on the explosion, the Chemical Safety and Hazards Investigation Board recommended that the American Institute of Chemical Engineers (AIChE) work with ABET, Inc., to establish additional curriculum requirements for the study of reactive chemical hazards.[8] A significant factor in the T2 explosion was the failure on the part of the company engineers and chemists to consider a higher-temperature reaction between the molten sodium metal and the 1,2-dimethoxy ethane used as the solvent.

It is evident that students should become aware of reactive hazards in classroom problems and discussions. That is the goal of this paper. We present an Euler's method kinetic model developed to improve the understanding of a decomposition reaction involving hydrogen peroxide that has resulted in two explosions in paper-mill bleach plants. As in the T2 incident, the engineers designing the peroxide bleach stage knew they were working with energetic chemicals and had a track record of safe use. As in the T2 incident, the design engineers had failed to consider all alternatives and, in particular, one specific reaction scenario resulting in a runaway reaction. The model presented here is critical to discovering the sequence of events that led to these explosions, and may be used as an example problem to help students learn about reactive hazards.

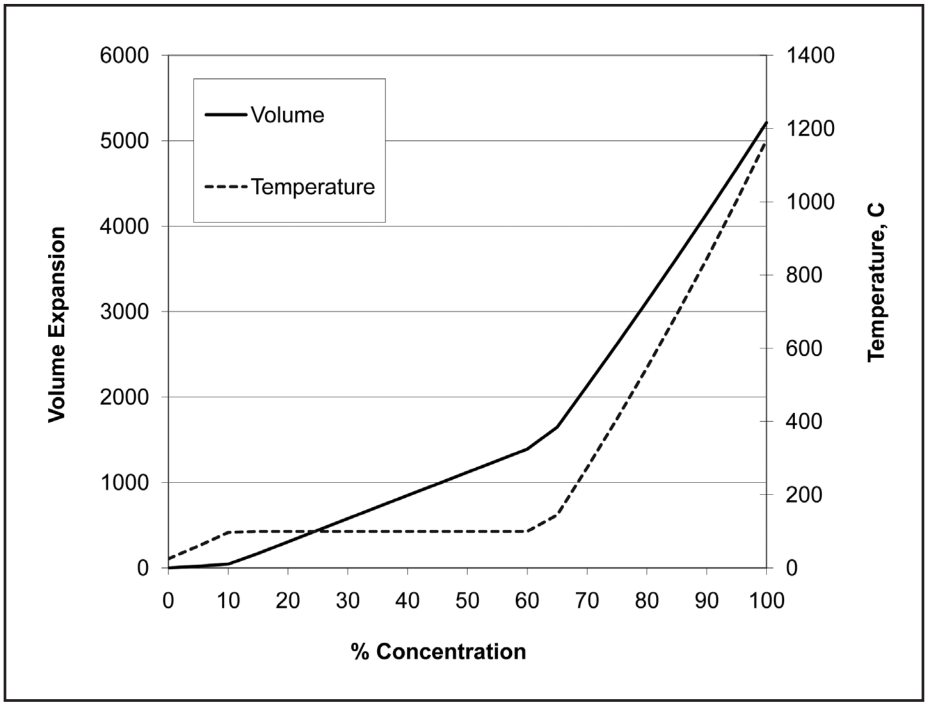

Figure 1. *Temperature and adiabatic volume of oxygen and steam resulting from decomposition of a single volume of hydrogen peroxide solution. Volumetric expansion is liters of gas produced per liter of peroxide solution.*

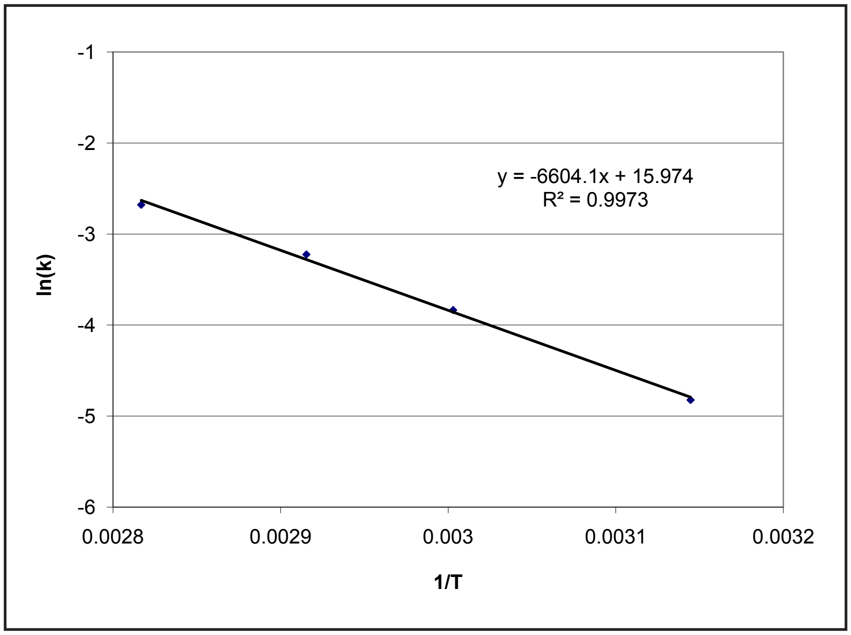

Figure 2. *Using the Arrhenius method to estimate the effect of temperature on kinetic rate constant. Data from Makkonen.[12] Temperature range of the data is 25 ℃ to 75 ℃ (298–348 K).*

PEROXIDE DECOMPOSITION

Peroxide is usually quite stable, decomposing very slowly at a rate less than 1% per year.[10] Under certain conditions, peroxide can decompose rapidly enough to cause process problems. The most serious peroxide accidents usually involve one of three types of decomposition processes: organic contamination; inorganic contamination; and alkali-induced decomposition. The normal (slow rate) decomposition, inorganic contamination, and alkali-induced decomposition are a disproportionation reaction producing oxygen and water according to the equation.[11,12]

$$2\ \mathrm{H_2O_2}(\mathrm{l}) \rightarrow 2\ \mathrm{H_2O}(\mathrm{g}) + \mathrm{O_2}(\mathrm{g}) \quad \Delta H = -59.8\,\mathrm{kJ/mol} \quad (1)$$

$$2\ \mathrm{H_2O_2}(\mathrm{l}) \rightarrow 2\ \mathrm{H_2O}(\mathrm{l}) + \mathrm{O_2}(\mathrm{g}) \quad \Delta H = -98.0\,\mathrm{kJ/mol}$$

This reaction is highly exothermic, and the resulting temperature rise increases the rate of decomposition—key conditions for a runaway reaction. The organic contamination reaction is an oxidation (combustion) process and is beyond the scope of this paper but certainly cannot be ignored. This type of reaction releases even more energy than the disproportionation reaction and was involved in both the sinking of the Kursk[4] and the Uniforêt mill transfer tank explosion.[9]

Using the ideal gas law and thermodynamic properties of hydrogen peroxide and water, the adiabatic volumetric expansion can be calculated for various concentrations of hydrogen peroxide (Figure 1). Gas volume is calculated by assuming complete decomposition into 1 mole of water and 0.5 mole of oxygen. Total heat is determined from the heat of reaction (98,073 J/mol H_2O_2 with product water in the liquid state). Thermal mass is determined by multiplying the oxygen gas produced times heat capacity (21.9 J/mol) and summing the water in the solution plus the water from decomposition and multiplying by the liquid phase heat capacity (75.6 J/mol). In a simple calculation, heat generated divided by thermal mass gives the estimated temperature rise. Once the temperature rise exceeds 75 ˚C (room temperature of 25 ˚C + 75 ˚C = 100 ˚C), the excess heat is divided by the heat of vaporization for water (40,657 J/mol) to determine the amount of water evaporated. Once the excess heat from decomposition is sufficient to vaporize all the water produced in the decomposition and evaporate all the water in the solution, the excess heat is used to raise the temperature of the gas above 100 ˚C.

Between the 0.5 moles of oxygen evolved and the water vaporized by the heat of decomposition, extremely large gas volumes can be produced. At about 10% peroxide concentration, the heat of decomposition raises the solution temperature from 25 ˚C to 100 ˚C, and decomposition begins to generate steam (Figure 1). At about 65% concentration, all the water is turned to steam and the temperature rises above 100 ˚C, causing thermal expansion of the gas.

ALKALI-CATALYZED DECOMPOSITION

Typical pulp-mill peroxide bleaching stages add peroxide and caustic into wood pulp suspended in water at 10% to 15% solids and flowing through a pump or mixer going to a bleaching tower. As long as the peroxide is diluted by pulp, the peroxide stage safely bleaches the pulp and the majority of the oxidizing potential of the peroxide is consumed in beneficial reactions with residual lignin. The problems have occurred when peroxide and caustic are added to a pump or piping system without dilution water or pulp flow.

To verify that the bleach plant explosions could have been caused by alkali-induced hydrogen peroxide decomposition, a kinetic model was developed to determine the rate of gas formation and likely pressure build-up in the peroxide reaction.

To verify that the bleach plant explosions could have been caused by alkali-induced hydrogen peroxide decomposition, a kinetic model was developed to determine the rate of gas formation and likely pressure build-up in the peroxide reaction. The kinetic expression was integrated in an Excel spreadsheet (Microsoft Corp., Redmond, Wash.) using Euler's method. The time step was varied depending on the rate of the reaction; 0.01 s per step was typical for faster reactions.

To calculate the pressure produced by peroxide decomposition, it is necessary to estimate the effect of temperature on reaction rate and the effect of pressure on boiling point of water. The second-order decomposition of peroxide depends on the concentrations of both the acid (HOOH) and base (HOO–) forms of peroxide. The rate equation as presented by Makkonen[12] is

$$dP/dt = -k\left[\mathrm{HOO^-}\right]\left[\mathrm{HOOH}\right] \qquad (2)$$

where P is total peroxide concentration and t is time. The apparent rate constant k is about 8×10^{-3} at 45 ˚C. The rate reported is an apparent rate because it is condition-dependent. Considerable variability in rates has been reported, and Makkonen reports slower decomposition for reactions stabilized with magnesium or silicate and faster rates for experiments with added transition metals.[12] Rate data from Makkonen[12] were plotted to determine the parameters in an Arrhenius rate expression (Figure 2). This method of estimating reaction rate incorporates obvious risks, but attempting to directly measure reaction rates of potentially explosive reactants under high-temperature pressurized conditions is challenging.

Equation for the Rate Constant (Figure 2)

$$k = e^{15.974 - 6604.1/T} \qquad (3)$$

Water boiling point and temperature data are readily available from a number of sources. Plotting the log of pressure against the inverse of absolute temperature provides a straight line relationship suitable for estimating the boiling point rise as pressure increases (Figure 3). Eq. (4) is the Antoine equation using absolute temperature and setting the value for C = 0. Because the rest of the kinetics is based on temperature in degrees Kelvin, this choice eliminates a unit conversion and provides a convenient estimate.

Modified Antoine Equation Estimating Maximum Temperature at Pressure (Figure 3)

$$\ln(\mathrm{kPa}) = \frac{-4931.2}{T} + 17.734 \tag{4}$$

$$T = \frac{4931.2}{17.734 - \ln(\mathrm{kPa})}$$

Steam and Oxygen Escape

The venting of steam and oxygen is estimated using the equations for flow and pressure in orifice meter/venturi or flow nozzle meters[13]:

$$V_l = C\sqrt{2g_c\frac{(P_h - P_l)}{\rho_h}} \tag{5}$$

where V_l is flow in velocity (m/s); C is a dimensionless constant with value less than 1, typically ranging from about 0.6 to 0.9; g_c is a dimensional constant = 1 m·kg/(N·s^2); ρ_h is the density of the gas on the high-pressure side of the orifice; and P_h and P_l are the pressures on the high- and low-pressure sides of the orifice, respectively. Assuming the gas expands to atmospheric pressure, P_l = 101 kPa. Calculating density using the ideal gas law, PV = nRT, water is 0.018 kg/mol, giving density as 0.018n/V = 0.018P_h/R/T; R = 8.314 m^3·Pa/K/mol, leaving

$$V_l = 30.39C\sqrt{2g_c\frac{(P_h - 101000)T}{P_h}} \tag{6}$$

Assuming C = 0.85 and a 4-in.-diameter pump suction, the cross-sectional area is 0.0081 m^2, volume loss is V_l · 0.0081 (m^3/s), and steam losses (in mol/s) are P_h · Vl ·0.0081/R/T_r, the net equation is

$$\frac{M}{s} = 0.0252\sqrt{2g_c\frac{(P_h - 101000)T}{T}} \tag{7}$$

where M is mass. There are a number of approximations in the model. First among these is the orifice constant, which is typically around 0.85. This constant is considered a good approximation for flow conditions below sonic velocity and where flow direction is in line with the orifice. Conditions during the pressure spike approach sonic velocity, and with the pump rotor turning, the direction of flow in the pump casing should be tangential—that is, perpendicular to the suction opening. The 0.85 value is used as a conservative estimate.

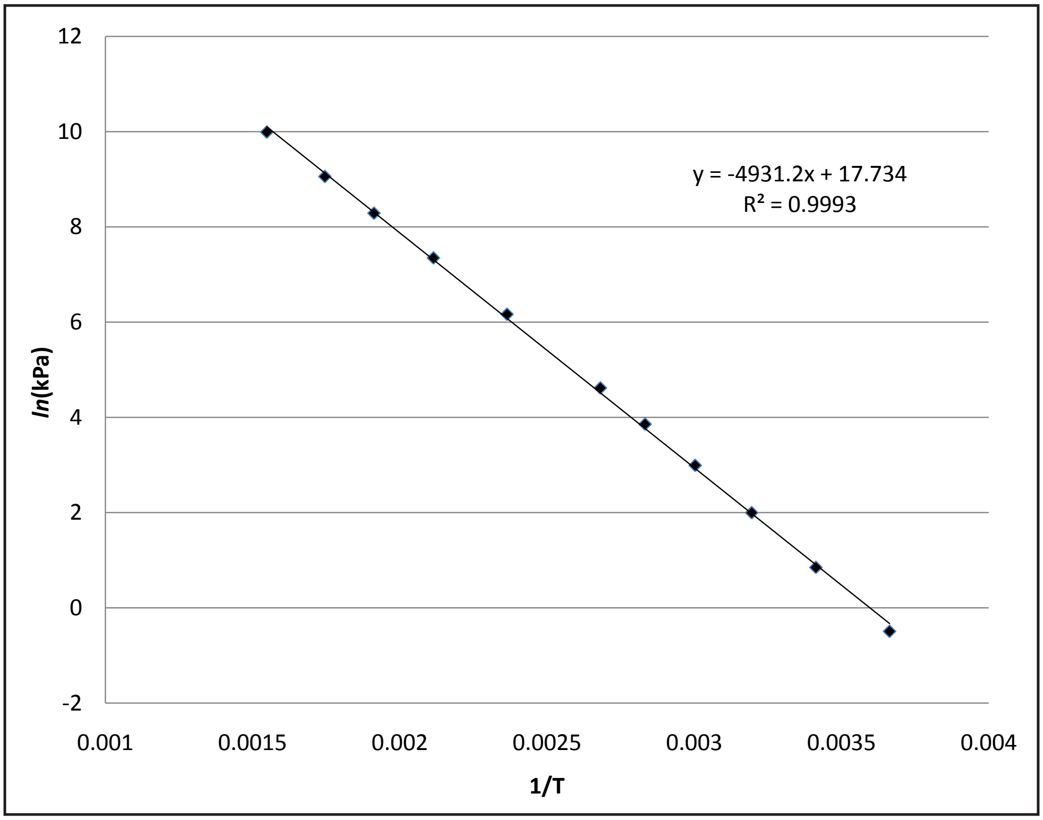

Figure 3. *Determination of the coefficients for the Antoine equation to estimate the relationship between the boiling point of water and pressure. Data from the* CRC handbook of Chemistry and Physics*, 76th Ed., Linde, D.R., ed., CRC Press, Boca Raton, FL, pp. 6-15–6-16 (1995).*

The base case model assumed peroxide and 25 wt% caustic were entering a pump with an internal volume of 99 L (3.5 ft^3). Heat loss was ignored. The peroxide flow rate was 2.5 L/min of 50% by weight hydrogen peroxide (14.7 molal), and the caustic flow rate was 1.23 L/min of 25% by weight sodium hydroxide (6.25 molal). These values represented operating conditions obtained from distributed control system (DCS) data recorded at the time of one of the explosions.

Various options were evaluated, including adiabatic conditions and gas-vented conditions. For the vented cases, gas flow was estimated using Eq. (7).[13] The model assumes no significant rate acceleration from pump surfaces or contaminants. Some scenarios required extrapolating the reaction rate to temperatures well beyond the temperature range evaluated by Makkonen[12] or found in the steam tables used to develop Eq. (4). The model does not correct for activity or change in pK_a with temperature. Errors introduced by these assumptions can be substantial. The value of the model is in demonstrating features of the decomposition process that can predispose the process to catastrophic decompositions, but not in identifying conditions that are certifiably safe.

With steady-state flows, the models did indicate the likelihood of a rapid increase in casing pressure when gas escape was not allowed, but when venting was included in the model, the predicted pressure build-up was minimal (Figure 4). In fact, under most conditions evaluated, the model predicted that the use of 50 wt% peroxide was safe.

Reviewing the DCS data and plant layouts, peroxide appeared to have been flowing into the pump casing for several minutes before the caustic entered the pump. When this scenario is tested (Figure 5) the pressure remains at atmospheric for the first

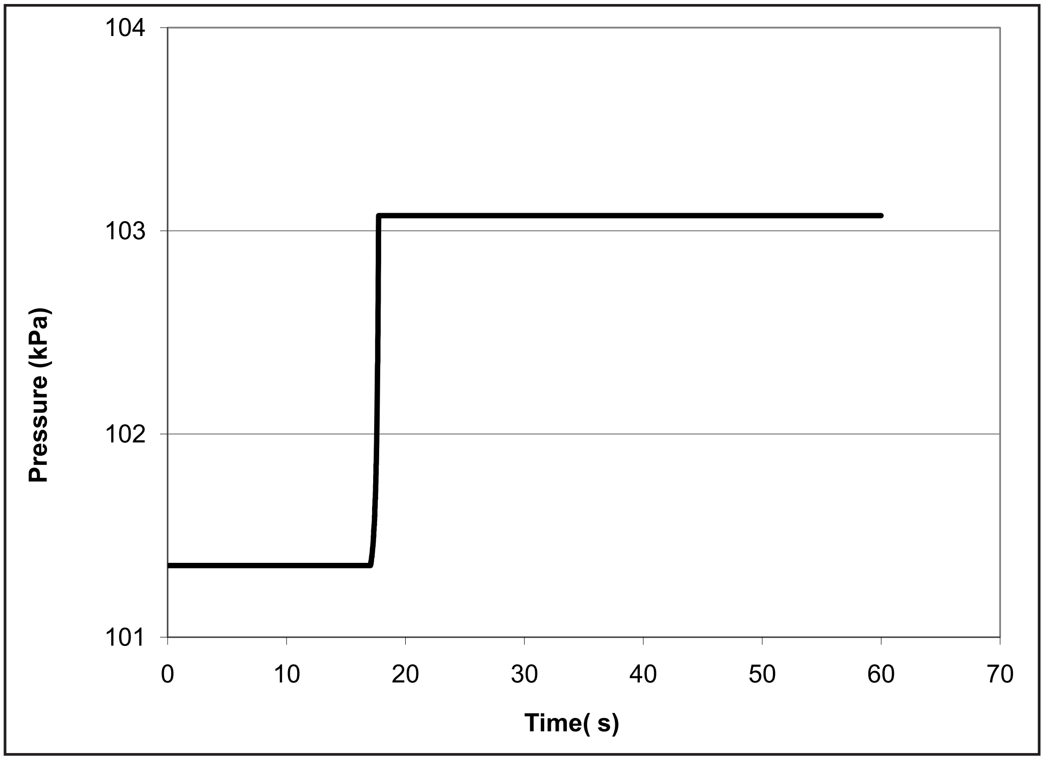

Figure 4. *Pressure vs. time for the steady-state flow case with 14.7 molal peroxide and 6.25 molal sodium hydroxide. The model assumes a 10-cm-diameter vent.*

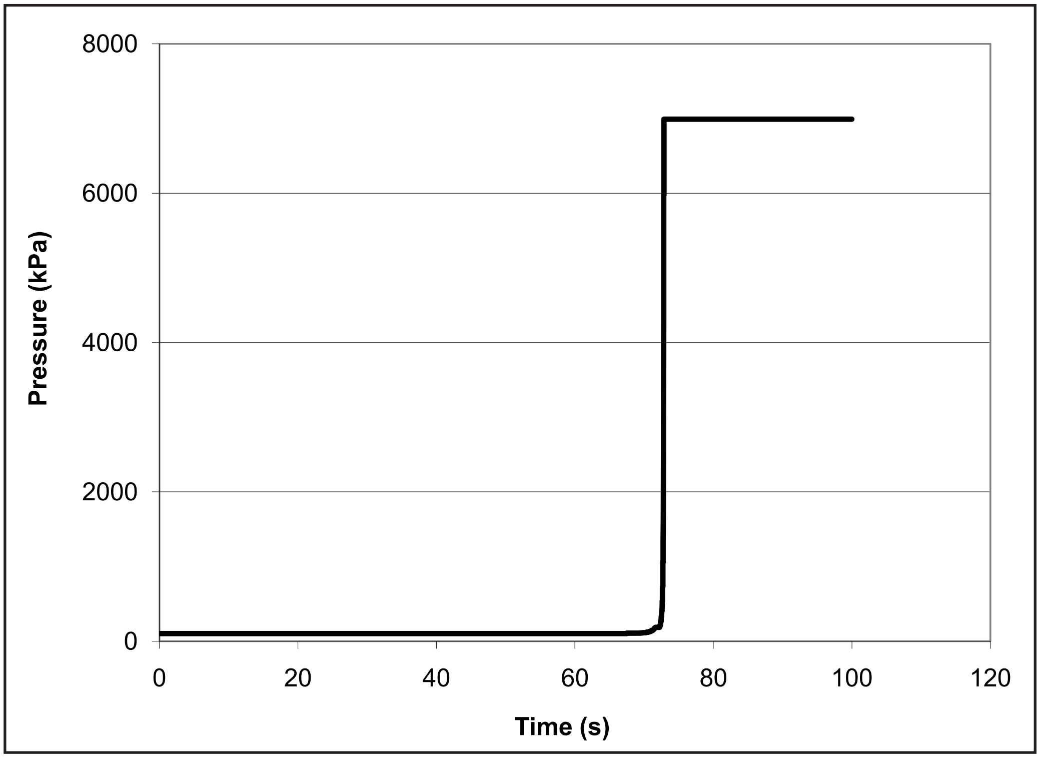

Figure 5. *Estimated pressure when the pump casing contained 25 L of 14.7 molal peroxide prior to the start of sodium hydroxide addition. The model assumes a 10-cm-diameter vent.*

70 s but then rises from 200 kPa to 6,695 kPa in 0.55 s. The temperature rises to 556 K at peak pressure, and this heat continues to boil water and maintain pressure after much of the peroxide has decomposed. The molar concentrations of $[H_2O_2]$ and $[HO_2^-]$ are shown in Figure 6 for the same model. The scenario shows a very rapid loss of peroxide, also at about 70 s. Because the reaction does not consume the alkali, the acid form decreases preferentially. In this case, the $[H_2O_2]$ concentration drops three orders of magnitude in less than a second. The critical contribution of peroxide in the pump is that the kinetic rate rises as caustic is added, and the HOO^- concentration increases. This sets up a condition in which kinetic rate is accelerating due to both the increase in temperature and the rapid approach to optimum reactant ratio.

This type of rapid pressure buildup within the partially confined space of a pump is sufficient to result in catastrophic failure. In one of the reported incidents, the explosion was so violent that pieces of debris were found up to a half-mile away from the original pump location. Shrapnel damaged the nearby bleach towers and surrounding equipment and instrumentation. Both pump explosions breached the adjacent peroxide bleach tower. For the scenario in Figures 5 and 6, peroxide flow started 10 min before caustic flow. The entire incident took less than 2 min after sodium hydroxide began flowing into the pump. Without the reservoir of peroxide in the casing, the decomposition reaction quickly consumes the peroxide in the acid form and the reaction rate slows dramatically. This results in substantially smaller predicted pressure increases.

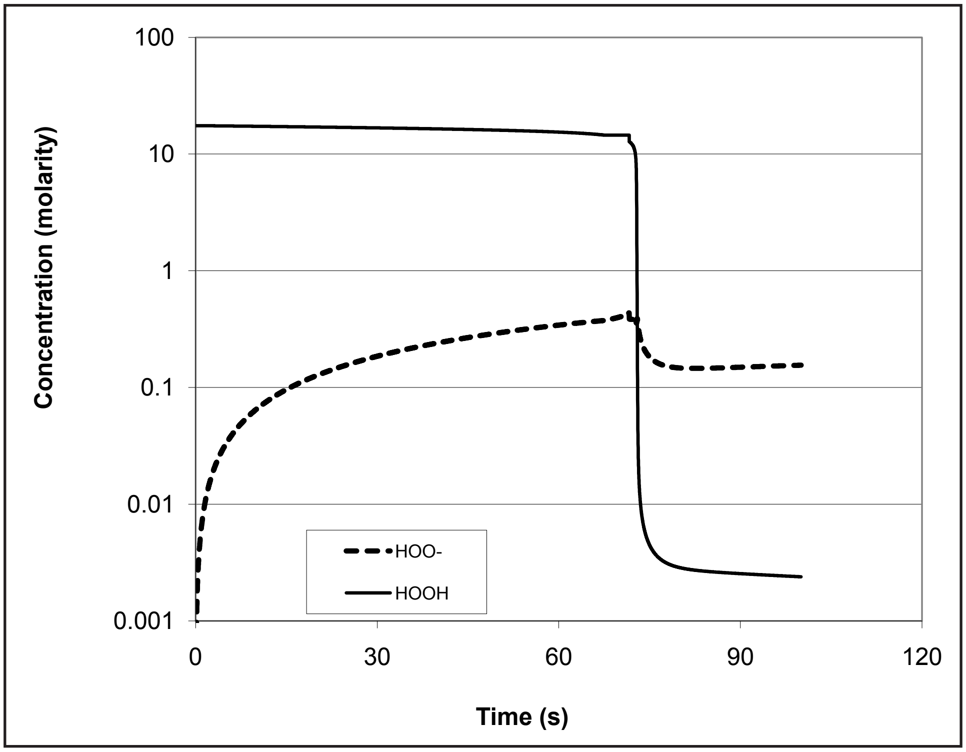

Figure 6. *Concentration of H_2O_2 and HO_2^- as estimated by the kinetic model.*

CONCLUSION

The bleaching processes that resulted in two peroxide explosions had been used safely by pulp mill bleach plants for years. When kinetic equations describing peroxide decomposition are used with typical steady-state operating conditions, no significant pressure rise is predicted. When the same kinetics are examined with peroxide flowing into the pump ahead of the caustic, a catastrophic pressure rise is predicted. Examination of startup and shutdown conditions and order of chemical addition, including potential system accumulation, is necessary to fully determine risks. Effectively, when using kinetic models to evaluate industrial operations, transient operational details are extremely important and can transform systems that had been operating safely into bombs. Truly, with peroxide bleach plants, the devil is in the details.

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