# Hydrogen Peroxide—An Environmentally Friendly but Dangerous Bleaching Chemical

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## ABSTRACT

Within the past 15 years, at least three bleach plants in North America experienced catastrophic equipment failures associated with the use of 50 wt% peroxide. People were badly injured in two instances, and these mills were fortunate to have avoided fatalities in these events. Hydrogen peroxide can be and has been used safely for many years, but like any strong oxidant, it must be handled with respect. This paper evaluates safety concerns associated with the use of hydrogen peroxide in the bleach plant. Several safety practices are suggested to address issues identified by these explosions and minimize the risk associated with use of peroxide.

## INTRODUCTION

The use of hydrogen peroxide in pulp bleaching has increased considerably over the past decade. It has been touted 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) in concentrations under 53 wt% and in quantities less than 7,500 pounds [3]. As such, many people assume that hydrogen peroxide is inherently safe. Contributing to this perception of safety is the fact that dilute hydrogen peroxide is sold in grocery and drug stores and has several topical usages (such as mouth washing, hair bleaching, and disinfecting minor cuts). At the higher concentrations employed in industry, hydrogen peroxide can be extremely dangerous. Disastrous events—from the sinking of the Kursk submarine [4] to explosions in tanks [2,5] and bleach plants [6,7]—have occurred due to hydrogen peroxide reactions.

The major safety problems related to hydrogen peroxide are the potential for rapid pressurization, the potential for fire due to oxygen formed in decomposition, and peroxide/organic vapor phase explosions. Peroxide at high concentrations may result in burns if allowed to come into contact with skin, but it typically reacts slowly with flesh and can be washed off before causing serious damage. Ingestion, however, may be fatal [8].

Over the past 15 years, at least three bleach plants within 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 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].

## PEROXIDE DECOMPOSITION

In general, peroxide is stable, decomposing very slowly at a rate less than 1% per year [10]. In storage tanks, even this slow decomposition creates risk. Assume that 20 tons of a 70% peroxide solution decomposing at the rate of 0.1% per year is stored in a sealed tank that is 95% full. After only 2 months of storage, the oxygen evolved from decomposition is sufficient to increase the pressure inside the tank by 14.7 lb/in$^2$. Most atmospheric storage vessels are not designed to withstand this level of pressure and would rupture. Safety relief vents of at least 200 cm$^2$ per tonne of 100% peroxide should be included on storage tanks [11] to allow adequate ventilation.

The most serious peroxide accidents usually involve one of three types of decomposition processes: organic contamination, inorganic contamination, and alkali-induced decomposition. The peroxide decomposition reaction is a disproportionation reaction producing oxygen and water according to the following equation [12,13]:

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

The normal (slow rate) decomposition, inorganic contamination, and alkali-induced decomposition all have this stoichiometry and heat of reaction. The reaction is highly exothermic, producing enough heat to boil the product water and heat or boil the dilution water. A rise in temperature increases the rate of decomposition, which can lead to a runaway reaction if heat buildup cannot be controlled.

Peroxide systems are very unforgiving of contamination. Nearly all transition metals catalyze peroxide decomposition. Trace concentrations of transition metals such as iron, copper, and manganese increase peroxide decomposition markedly [11]. Suppliers stabilize peroxide to prevent trace quantities of metal impurities from accelerating decomposition. Decomposition is very rapid at most metal surfaces and large volumes of gas can be generated very rapidly if objects get into the peroxide storage or handling equipment. A rusty bolt will set up a steady stream of oxygen gas limited only by the surface area of the object. Because of the increased surface area, rough surfaces, such as the inside of a cast pump casing, also increase the decomposition rate [12].

Using first principle thermodynamics, the ideal gas law, and the decomposition reaction of peroxide, adiabatic volumetric expansion can be calculated for various concentrations of hydrogen peroxide. The effect of peroxide concentration on temperature and volumetric expansion from hydrogen peroxide decomposition is shown in Figure 1. Between the 1.5 mol of gas evolved from the direct decomposition reaction and the additional water vapor produced from the heat of decomposition, extremely large volumes of gas can be produced. At lower hydrogen peroxide concentrations, larger volumes of water need to be heated up before steam is generated. Thus, a considerable portion of the heat of decomposition is consumed as sensible heat and does not result in the production of steam. The model assumes the water produced by the decomposition remains liquid until the temperature reaches 100°C. At about 10% peroxide concentration, there is enough heat in the decomposition to raise the solution temperature from 25°C to 100°C, and decomposition begins to generate steam. At about 60% concentration, there is no longer enough water in the solution to carry away the heat of reaction as steam, and the temperature rises above 100°C, causing thermal expansion of the gas.

Normally, contamination implies small amounts, and this usually prevents catastrophic accidents. The vents on peroxide tanks are oversized to prevent ruptures with small amounts of metal contamination. The use of vented ball valves in the piping system also helps to prevent pockets of peroxide from being trapped within the system [14].

Contamination by organic substances is even more hazardous. The reaction products in this case are $CO_2$ and $H_2O$, just as in combustion. The heat of reaction is from both the reduction of peroxide to water and the oxidation of carbon and hydrogen to $CO_2$ and $H_2O$. This is an even more energetic reaction than the disproportionation reaction catalyzed by alkali or metals. High-concentration hydrogen peroxide has been used as the oxidant in rockets and was the oxidant used in torpedoes on the Russian Submarine Kursk. When one of these torpedoes started to leak, the Kursk was doomed [4]. This type of reaction of high-concentration peroxide with a high-concentration organic substance resulted in a spectacular tank failure at the Port Cartier, Quebec, mill in 1993. A tank truck mistakenly started unloading diethylene triamine pentaacetic acid (DTPA) solution into a tank that still contained some 50% peroxide. The resulting explosion tore the tank away from the base and propelled it 400 ft to a landing in the mill's aeration lagoon.

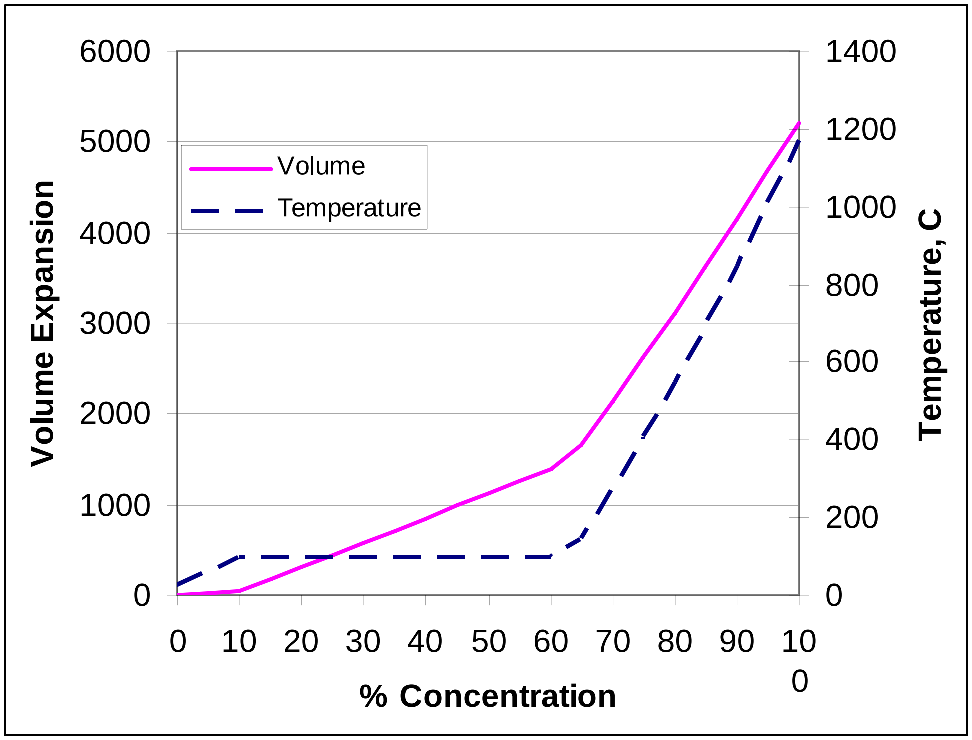

Figure 1. Temperature and adiabatic volume of oxygen and steam resulting from the decomposition of a single volume of hydrogen peroxide solution. Volumetric expansion is liters of gas produced per liter of peroxide solution.

## ALKALI-CATALYZED DECOMPOSITION

Alkali-induced hydrogen peroxide decomposition has the same stoichiometry and heat of reaction as the disproportionation reaction catalyzed by trace metals. Alkali-induced autocatalytic decomposition of hydrogen peroxide is a well-established second-order kinetic reaction [13]. Typical peroxide bleaching stages add peroxide and caustic into pulp that is flowing through a pump and/or mixer going into a bleaching tower. As long as the pulp is present and flowing, there is no particular safety problem. The peroxide stage performs pulp bleaching in a safe manner, and the majority of the oxidizing potential of the peroxide is consumed in beneficial reactions with residual lignin. The problem results when peroxide and caustic end up in a pump or piping system and there is no water or pulp flow to dilute the peroxide and absorb reaction heat. The second-order rate equation depends on both the acid (HOOH) and base ($HOO^-$) forms of peroxide:

$$\delta P/\delta t = k[HOO^-][HOOH]$$

where $P$ is peroxide concentration and $t$ time. The apparent rate constant $k$ is about $8 \times 10^{-3}$ at 45°C and follows the Arrhenius theory with an activation energy of 13.1 kcal/mol [13]. The rate reported is an apparent rate since it is condition dependent. There is considerable variability in reported rates, and Makkonen reports slower decomposition for reactions stabilized with magnesium or silicate and faster rates for experiments with added transition metals [13].

## ALKALI-CATALYZED DECOMPOSITION MODEL

The kinetic rate was programmed into an Excel (Microsoft Corp., Redmond, Washington) based time increment model to evaluate various scenarios potentially leading to explosive decomposition. The basic model assumed 50% peroxide and 25% caustic were entering a pump with an internal volume of 99 L (3.5 $ft^3$). The peroxide flow rate was 2.5 L/min, and the caustic flow rate was 1.23 L/min.

Various options were evaluated including adiabatic conditions and pressure-vented conditions. For the pressure-vented cases, pressure release was estimated assuming the orifice plate square root relationship between mass flow and differential pressure [15] and a 10-cm-diameter orifice (see Appendix).

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

where $M$ is mass, $P_\mathrm{h}$ pressure at the high-pressure side of the orifice, and $T$ temperature in kelvins. 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, but it needs to be understood that the gas release could be significantly constrained by the high flow rate and/or flow alignment and the model may not predict pressure spikes under some conditions where they would occur. The model also assumes no significant rate acceleration from pump surfaces or contaminants and estimates kinetic rate at temperatures well beyond the range evaluated by Makkonen [13]. The errors in these assumptions can be substantial. The value of the model is in demonstrating features of the decomposition process that can lead to catastrophic failures, but not in identifying conditions that are certifiably safe.

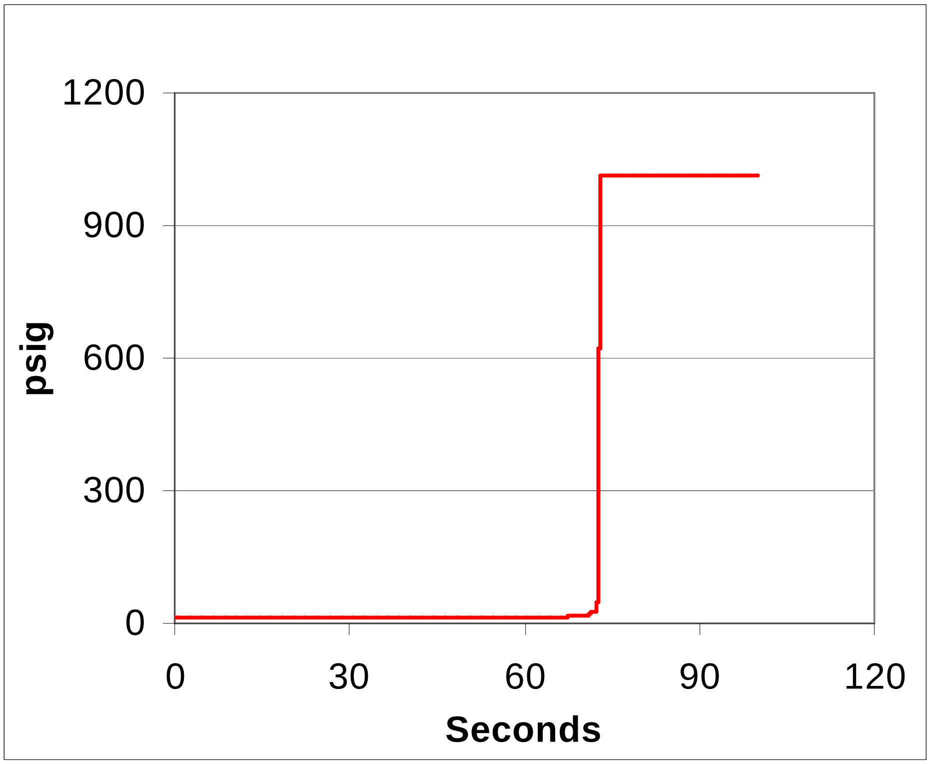

Figure 2. Estimated pressure for a scenario using 50% peroxide and 25% sodium hydroxide. The casing contained 25 L of peroxide prior to alkali addition and a 10-cm vent orifice.

The model does not show an explosive rise in pressure under most of the conditions evaluated. To obtain a significant spike in pressure, the model required the pump to contain some peroxide before the caustic was added. This precondition did occur in both mill explosions for which we have a reliable process record and was caused by circumstances that allowed the peroxide flow to reach the pump in advance of the caustic. The critical contribution of peroxide in the pump is that the kinetic rate rises as caustic is added, and the ratio of [HOOH] to [$HOO^-$] approaches 1. This sets up a condition where kinetic rate is accelerating due to both the increase in temperature and the rapid approach to the optimum reactant ratio.

An example of the pressure rise predicted by the kinetic model is shown in Figure 2 over a 2-min reaction time. Pressure remains at atmospheric for the first minute but then rises from 60 lb/in$^2$ to 1,000 lb/in$^2$ in 1.2 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 3 for the same model. The model 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 until concentration drops low enough to slow down the reaction. In this case, the peroxide concentration drops three orders of magnitude in less than a second.

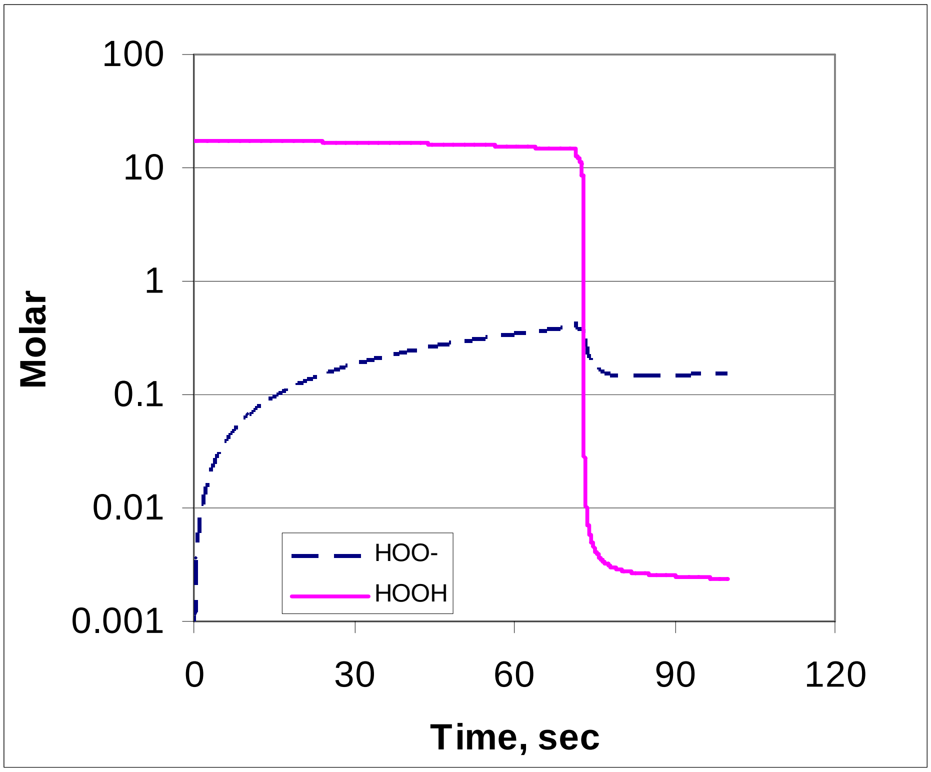

Figure 3. Concentrations of $H_2O_2$ and $HO_2^-$ as estimated by the kinetic model.

This type of rapid pressure buildup within the partially confined space of a pump is sufficient to result in catastrophic failure. Shrapnel is sent flying through nearby bleach towers and surrounding equipment and instrumentation. Both pump explosions breached the adjacent towers. For the scenario in Figures 2 and 3, the peroxide flow started 10 min before caustic flow. The entire incident took less than 2 min after sodium hydroxide began flowing into the pump. This bleach stage would have disintegrated about 12 min after startup. 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.

Potential safety measures to reduce risks associated with peroxide decomposition include (1) a reduction of peroxide strength from 50% to less than 10% and (2) interlocking peroxide flow to a flow meter placed at the pump or mixer. Interlocking to bleach plant production would not be sufficient because the line can operate for a half hour or more without instrumental indication that there is no flow at the peroxide mixer. Both mills had interlock control to a flow meter on the first stage of the bleach plant. Using 10% peroxide in the model, there is no significant pressure buildup in the pump out past the point of maximum kinetic rate ([HOOH] = [$HOO^-$]). The pump casing also filled with water after about 4 min of peroxide flow, and the vortex vacuum system would be extracting peroxide from the pump as fast as it was supplied. Reducing the peroxide concentration does not entirely eliminate the risks associated with the use of hydrogen peroxide. There are reports of equipment ruptures or explosions at this lower concentration. This step may reduce the risk but cannot completely prevent it.

## OXYGEN AND IGNITION

Additional peroxide safety risks result from one of the normal decomposition products, oxygen. When peroxide decomposes, the atmosphere becomes oxygen enriched, resulting in a significant reduction in the initiation energy required for a material to burn. This is a particular concern in the tops of storage towers where the oxygen can be expected to accumulate. Peroxide is such a powerful oxidizer that at high concentrations it will set other materials on fire. Usually this type of fire will not start on wet materials but is a greater risk when organic materials such as wood or pulp are dry. Hydrogen peroxide boils at 152°C and can increase in concentration significantly as the water evaporates. Great care is required when cleaning up spills to ensure that all pulp and other organic materials are thoroughly washed and the residual peroxide concentration is sufficiently diluted to decompose or evaporate before the material becomes dry.

## CONCLUSIONS

In general, hydrogen peroxide can be used safely in bleach plants. Ideally, significant levels of engineered protection are in place and the peroxide is being used at 10 wt% concentration or less. Care is always required. Typical pressure bursts tend to occur on startups or shutdowns. Higher concentrations increase the probability of a pressure burst and the violence of the event. These pressure bursts can result in catastrophic loss of equipment and are extremely hazardous to nearby personnel. Peroxide is a powerful oxidizing agent and can easily ignite other materials. Several examples of peroxide-initiated fires have been documented [2]. This is particularly important to consider when handling spills. Although it can be safely washed up with water, sufficient dilution must be provided to ensure the peroxide decomposes before the area dries, and care must be taken to make sure the entire area is cleared of the spilled peroxide and the pulp [5].

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## APPENDIX

Figure 1 is calculated by converting the peroxide concentration to moles and 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 $H_2O_2$), and thermal mass is determined by multiplying the oxygen gas produced by its heat capacity (21.9 J/mol) and summing the water in the solution plus the water from decomposition (as moles) times its heat capacity as a liquid (75.6 J/mol). Heat generated divided by thermal mass gives the estimated temperature rise. Once this 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. Thermal mass of oxygen and water vapor (36.7 J/mol) are summed and divided into the excess heat to get the temperature increase, which is added to the 100°C. Using the total moles of gas (water plus oxygen) and the temperature determined from the excess heat and thermal mass, the gas volume is determined using the ideal gas law and assuming atmospheric pressure. The graph shows that at about 10% concentration, there is sufficient heat to raise the solution to 100°C and start boiling water. At just over 50% concentration, there is no longer enough water to absorb the heat of reaction as steam, and the gas temperature starts rising and with it the gas pressure rises at a faster rate.

**Equation for Rate Constant** (Figure A-1)

$$k = e^{15.974 - 6604.1/T}$$

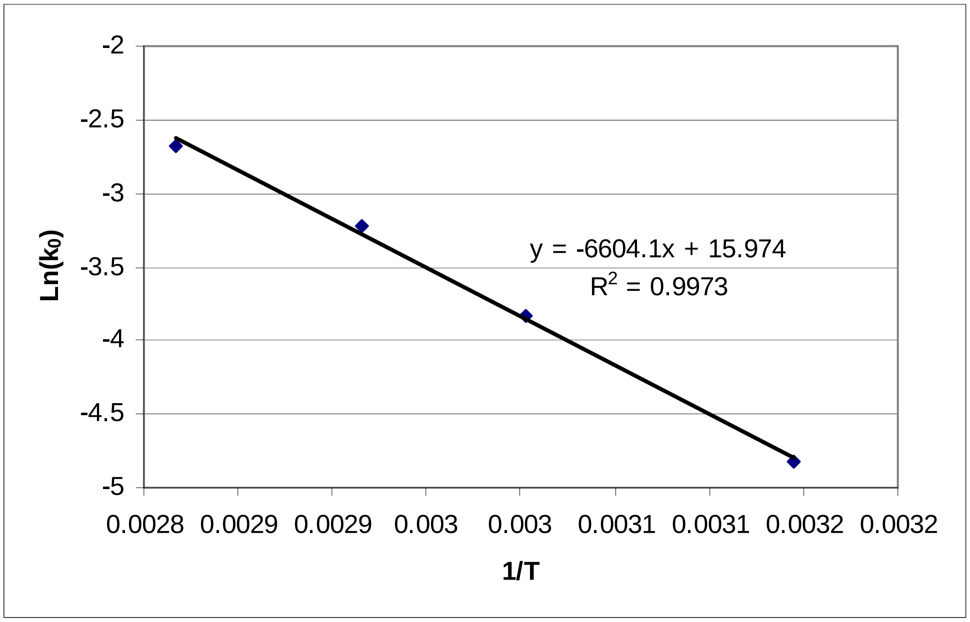

Figure A-1. Equation for effect of temperature on kinetic rate constant. Data from Makkonen [13]. Temperature range of the data is 25 to 75°C.

**Equation estimating maximum temperature at pressure** (Figure A-2)

$$\ln(\text{psia}) = \frac{-4940.5}{T} + 15.825$$

$$T = \frac{4940.5}{15.825 - \ln(\text{psia})}$$

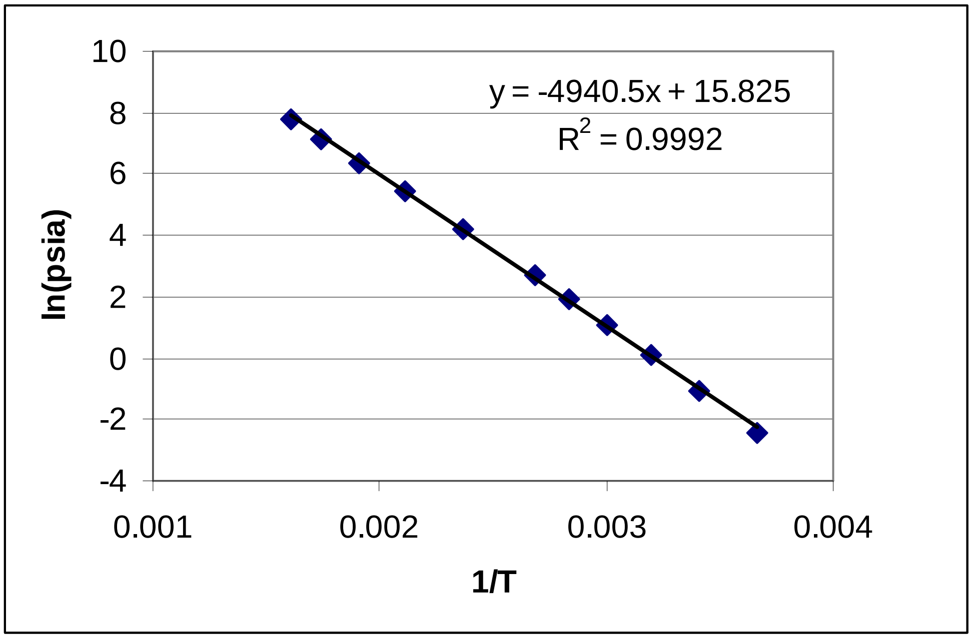

Figure A-2. Equation to estimate the dependence of the water boiling temperature relative to pressure. Data from CRC Handbook of Chemistry and Physics, 76th Edition, Linde, D.R., ed, CRC Press, Boca Raton, FL, 1995, pp 6-15 & 6-16.

**Steam and Oxygen Escape**

Venting of steam and oxygen is estimated using the equations for flow and pressure in orifice meter/venturi or flow nozzle meters:

$$V_{\text{l}} = C\sqrt{2g_{\text{c}}\frac{(P_{\text{h}} - P_{\text{l}})}{\rho_{\text{h}}}}$$

where $V_{\text{l}}$ is flow in velocity (m/sec); $C$ is a dimensionless constant with value less than 1 and typically ranging from about 0.6 to 0.9; $g_{\text{c}}$ is a dimensional constant at 1 m·kg/(N·$\text{s}^2$); $_{\text{h}}$ is the density of the gas on the high-pressure side of the orifice; and $P_{\text{h}}$ and $P_{\text{l}}$ are the pressures on the high- and low-pressure sides of the orifice, respectively. Assuming the gas expands to atmospheric pressure, $P_{\text{l}}$ = 101 kPa; calculating density using the ideal gas law, $PV = nRT$, water is 0.018 kg/mol, giving density as 0.018,·$n/V = 0.018P_{\text{h}}/R/T$; $R$ = 8.314 $\text{m}^3$·Pa/K/mol, leaving

$$V_{\text{l}} = 30.39C\sqrt{\frac{(P_{\text{h}} - 101000)T}{P_{\text{h}}}}$$

Assuming C = 0.85 and a 4-in.-diameter pump suction, the cross-sectional area is 0.0081 $\text{m}^2$ and volume loss is $V_{\text{l}}$ · 0.0081 ($\text{m}^3$/sec) and steam losses (in mol/s) are $P_{\text{h}}$ · $\text{V}_{\text{l}}$ ·0.0081/$R$/$T_{\text{r}}$, the net equation is

$$\frac{M}{\text{s}} = 0.0252\sqrt{\frac{(P_{\text{h}} - 101000)P_{\text{h}}}{T}}$$

# Peroxide: An Environmentally Friendly but Dangerous Bleaching Chemical

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# $H_2O_2$

- When properly handled, peroxide is an efficient and effective bleaching chemical.
- The product of the peroxide reaction is typically water but it can also form oxygen and participates in substitution reactions where it forms alcohol functional groups.
- As a high concentration solution, it is easy to handle and distribute in the mill.

# Hydrogen peroxide

- Hydrogen peroxide is typically shipped as 50% or 75% solutions and is normally stored in the mills at 50%.
- As received and if properly stored, it is quite stable, decomposing at less than 1% per year.
- Storage and handling equipment do need to be equipped with proper vents to release the oxygen gas formed in decomposition.

# But - energy is everything

| | Energy, KJ/g | Gas release ml/g |
|---|---|---|
| $H_2O_2$ | 1.7 | 1090 |
| $ClO_2$ | 1.4 | 520 |
| Trinitrotoluene | 2.0 | 813 |

# Peroxide concerns

- It is a strong oxidant like chlorine and chlorine dioxide.
- It can decompose to oxygen and lower ignition temperatures.
- It can serve as the oxidant source for combustion at high concentrations.
- It gives off a lot of heat and gas when it decomposes.

# Peroxide handling

- Everything contacting concentrated peroxide must be scrupulously clean – free of organic and inorganic contamination.
- Suitable metallurgy is aluminum or stainless steel.
- Best to “pickle” tanks and pipes before start-up, or start with a dilute peroxide solution to passivate the surfaces.

# Peroxide safety concerns

- Organic contamination
- Case Study: Port Cartier
- Inorganic contamination
- Spills and cleanup
- Pressure spikes
- Case studies: Prince George and Evadale

# Organic contamination

- Peroxide oxidizes organic materials to $CO_2$ and water.
- Concentrated peroxide is used as the oxidant in rocket and torpedo propulsion systems.
- The energy given off is the enthalpy of combustion of the organic material plus stored energy in the peroxide.
- Peroxide decomposition results in high steam and gas volumes and can produce runaway reactions.

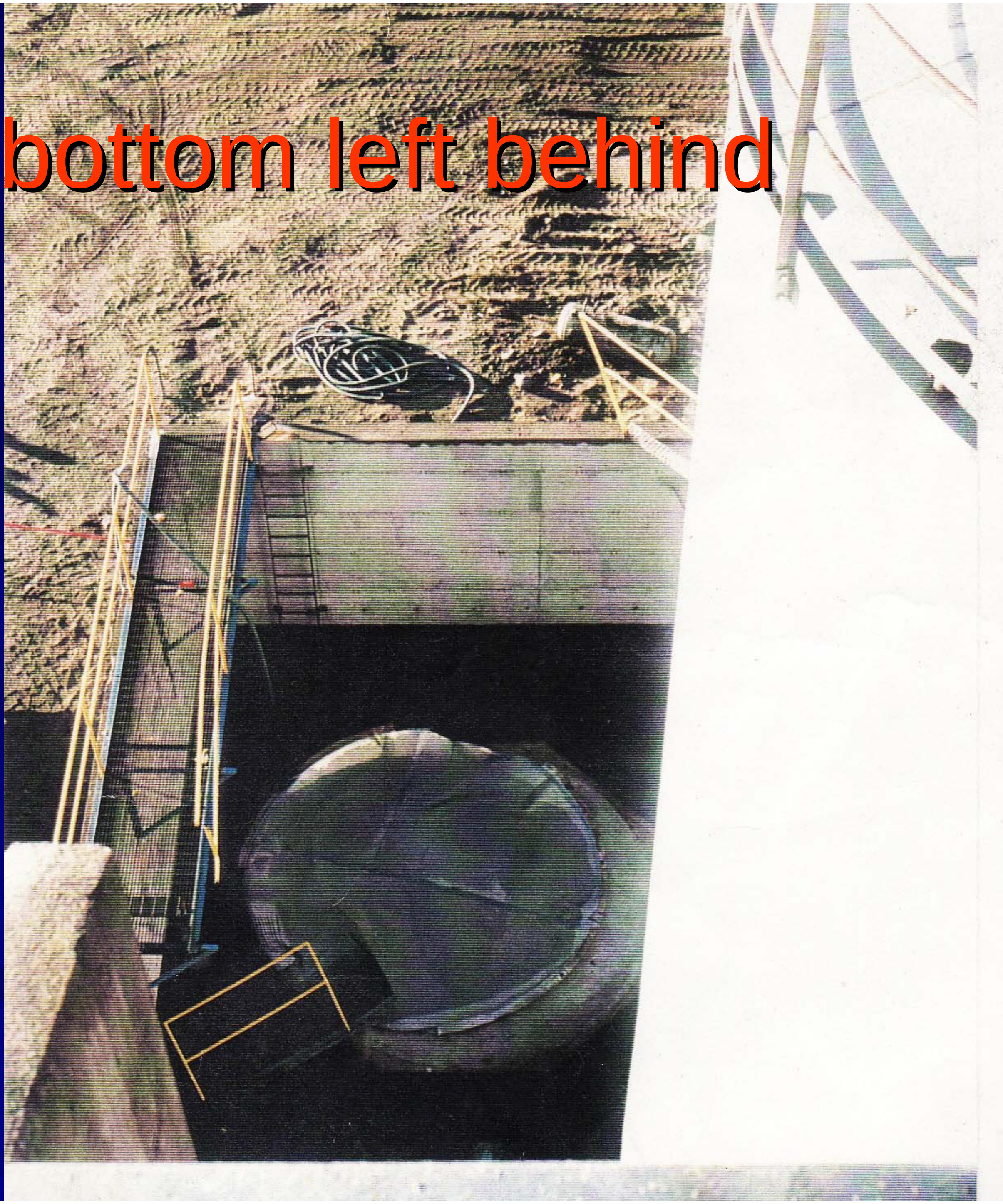
# Examples of organic contamination

- Port Cartier.
- Russian submarine Kursk.
  - peroxide leak from a torpedo (note, the cause of this explosion is thought to have been a peroxide leak and it very likely involved organic materials like grease and clothing. Once released in this manner – inorganic contamination is also probable.)
- Allied signal.
  - Wastewater tank and peroxide.

# Case study: Port Cartier

- A tank truck of DTPA was mistakenly unloaded into a transfer tank that had previously handled 50% peroxide.
- The tank level detector registered zero but because of the location of the dp cell, the tank could have contained as much as 2650 liters of 50% peroxide.
- About 30 minutes after the unloading process started, the tank exploded or more accurately rocketed 400 feet, landing in the aeration lagoon.

# Tank bottom left behind



# The transfer tank ended up here

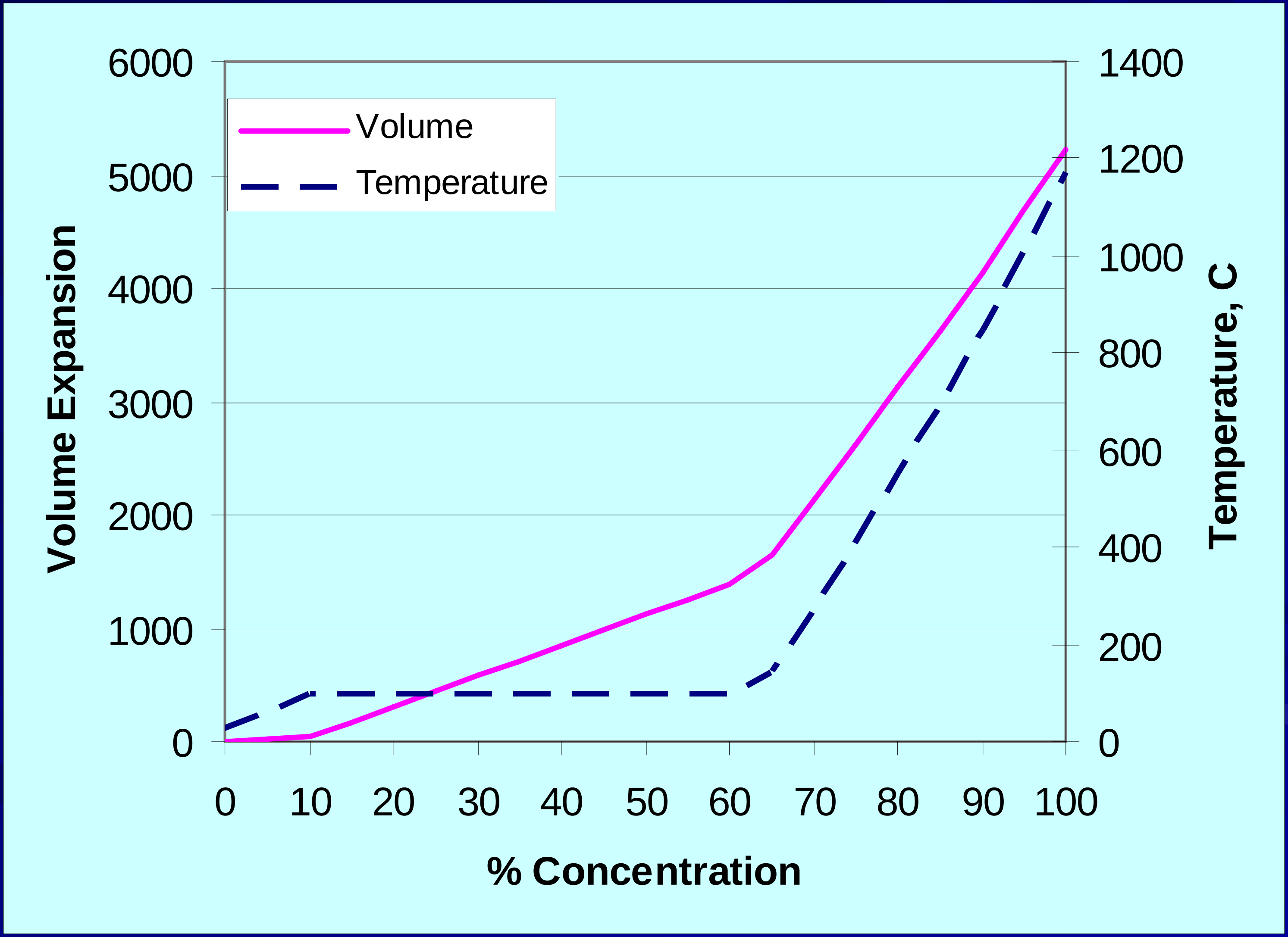
# The tank – looking back towards the mill

# Inorganic and Alkali Induced Decomposition

# Peroxide decomposition

- $2H_2O_2 \rightarrow 2H_2O_{(g)} + O_2$
- 14.3 kcal/mole
- Sufficient exotherm to vaporize the product water and above 10% weight concentration, boil the dilution water.
- Above 60% weight concentration, there is enough reaction heat to vaporize all dilution water.

# Volumetric expansion

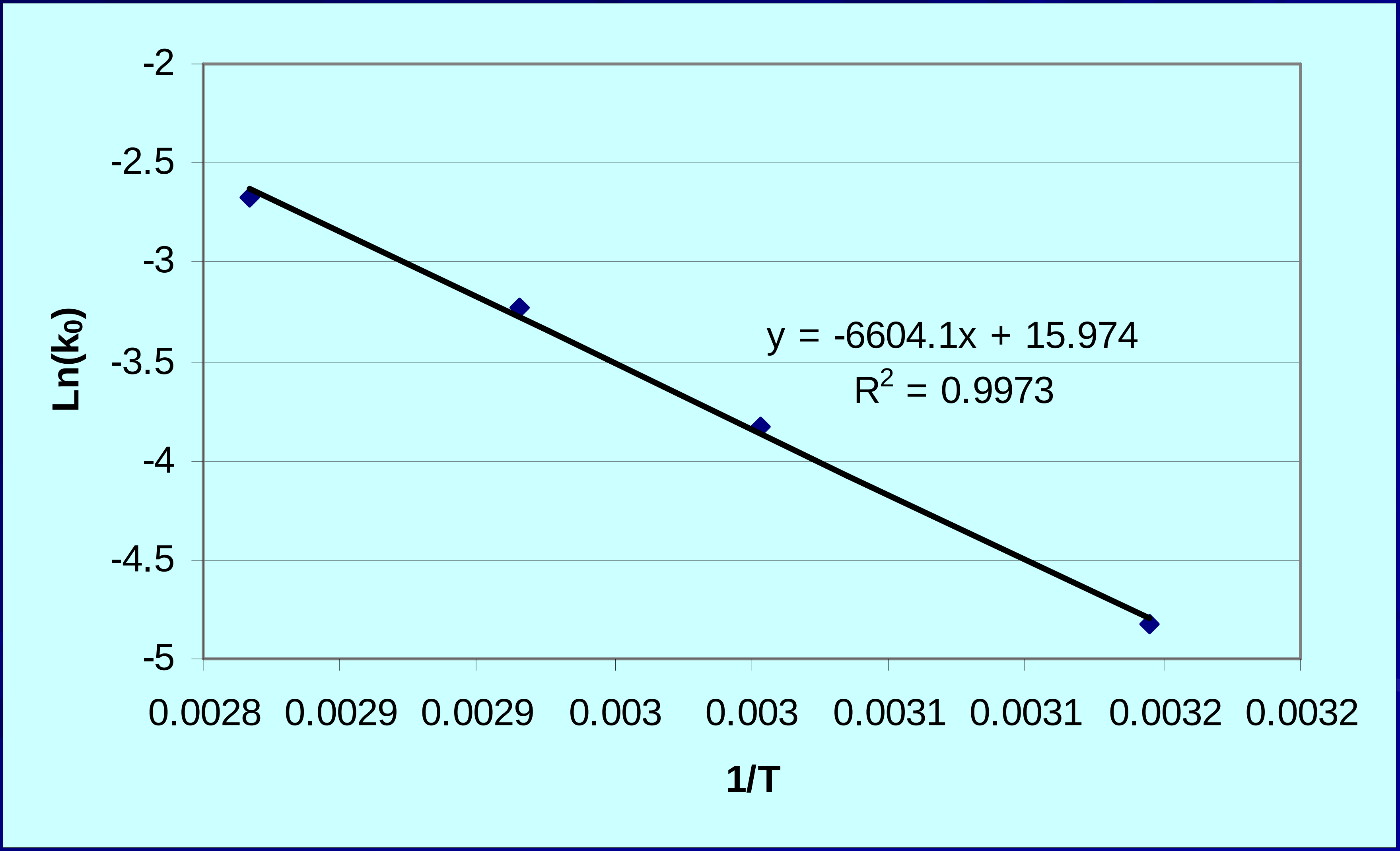


# Kinetics of alkaline decomposition

- Kinetics known for “clean” systems.
- $H_2O_2 + HO_2^- \rightarrow H_2O + OH^- + O_2$
- $d[P]/dt = k[H_2O_2][HO_2^-]$.
- Kinetics follows Arrhenius theory giving an activation energy of 13.1 kcal/mole.
- Rates are apparent rates because decomposition is slowed by addition of chelating chemicals.

- Makkonen, Ph.D. Thesis, University of Washington, 1971.

# Peroxide kinetics



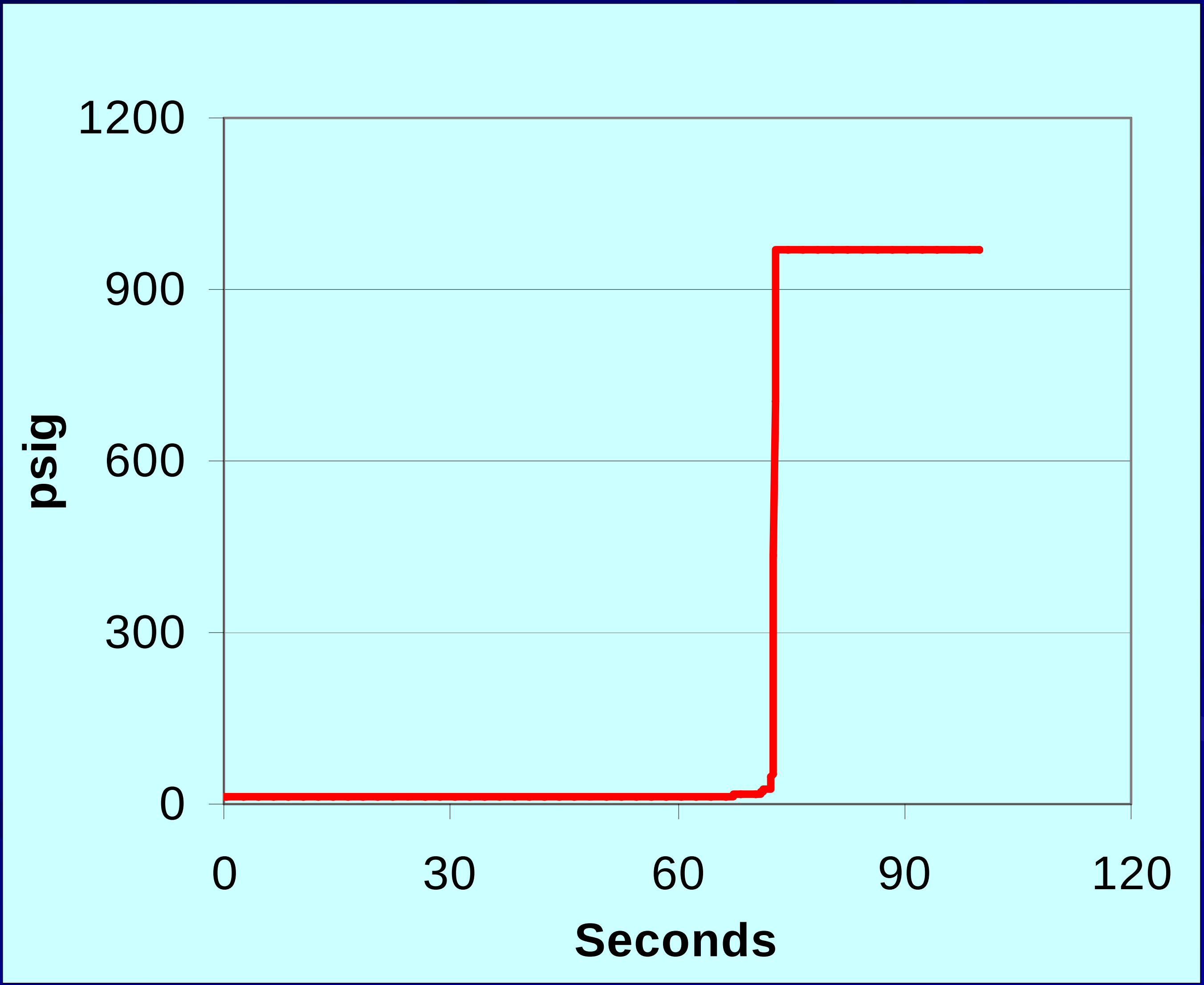
# Kinetic model: pieces

- Time increment model (0.01 second)
- Reaction rate
- Reaction heat
- pH equilibrium ($H_2O_2$ and $HO_2^-$)
- Estimate of boiling point and pressure
- Estimate of gas escape (orifice plate model)

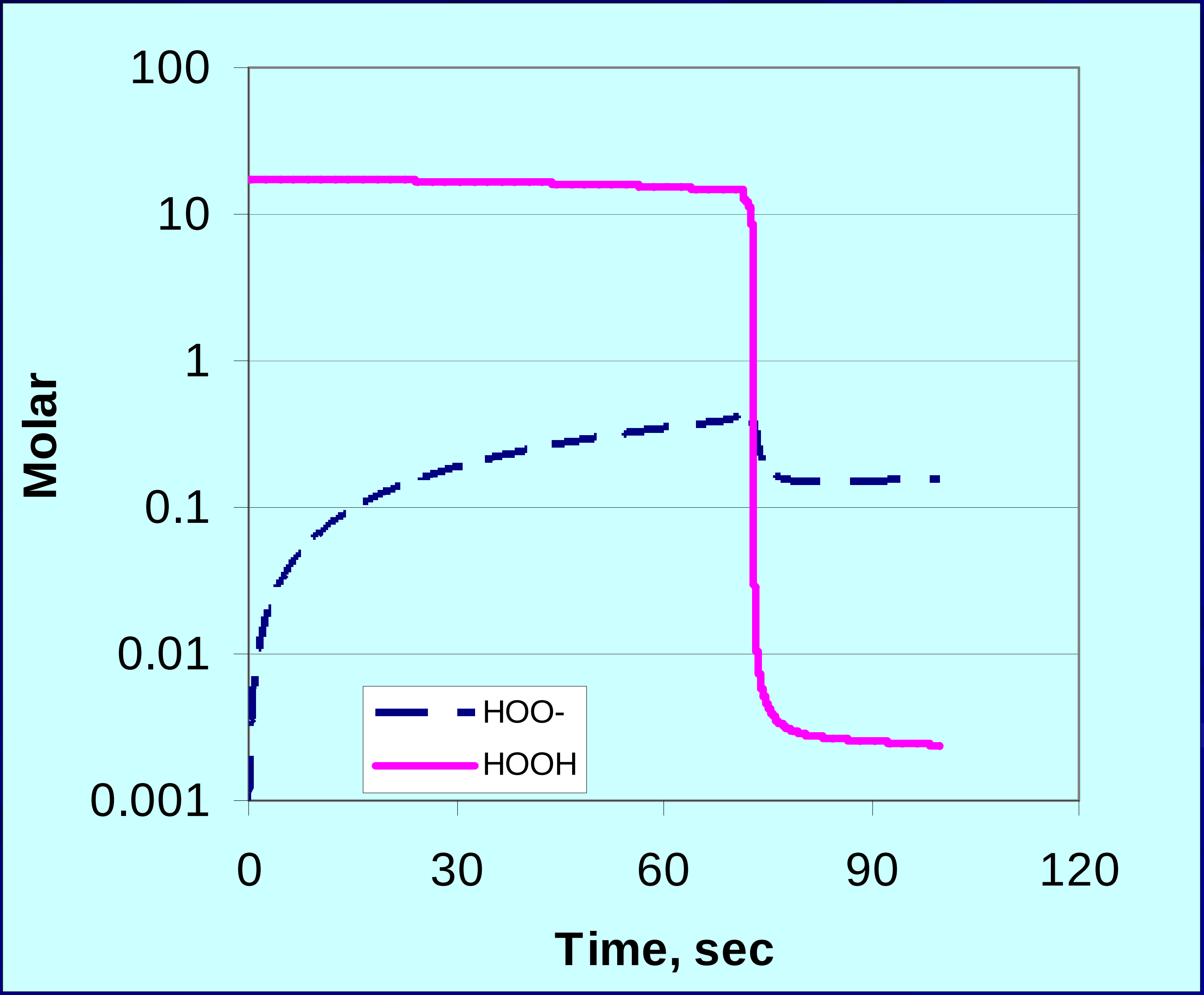
# The cautions: The assumptions

- Kinetics continues to follow Arrhenius model beyond the temperature tested.
  - When does diffusion become limiting?
- Model for gas release
  - too little gas? Too much gas?
  - Sonic velocity?
  - Effect of rotor forced flow alignment
- pKa relative to temperature?
- Vacuum assist

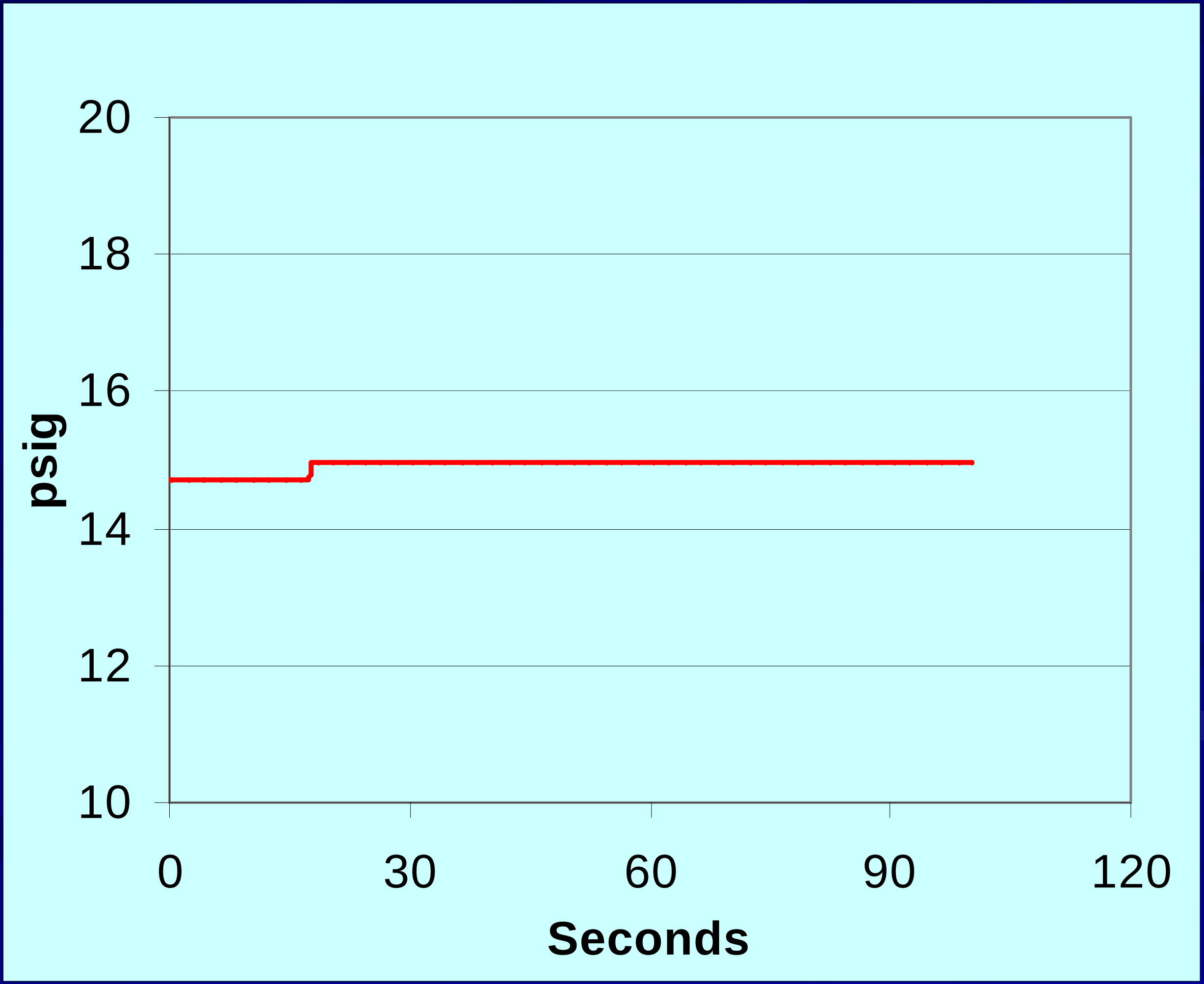
# Pressure with preloaded peroxide



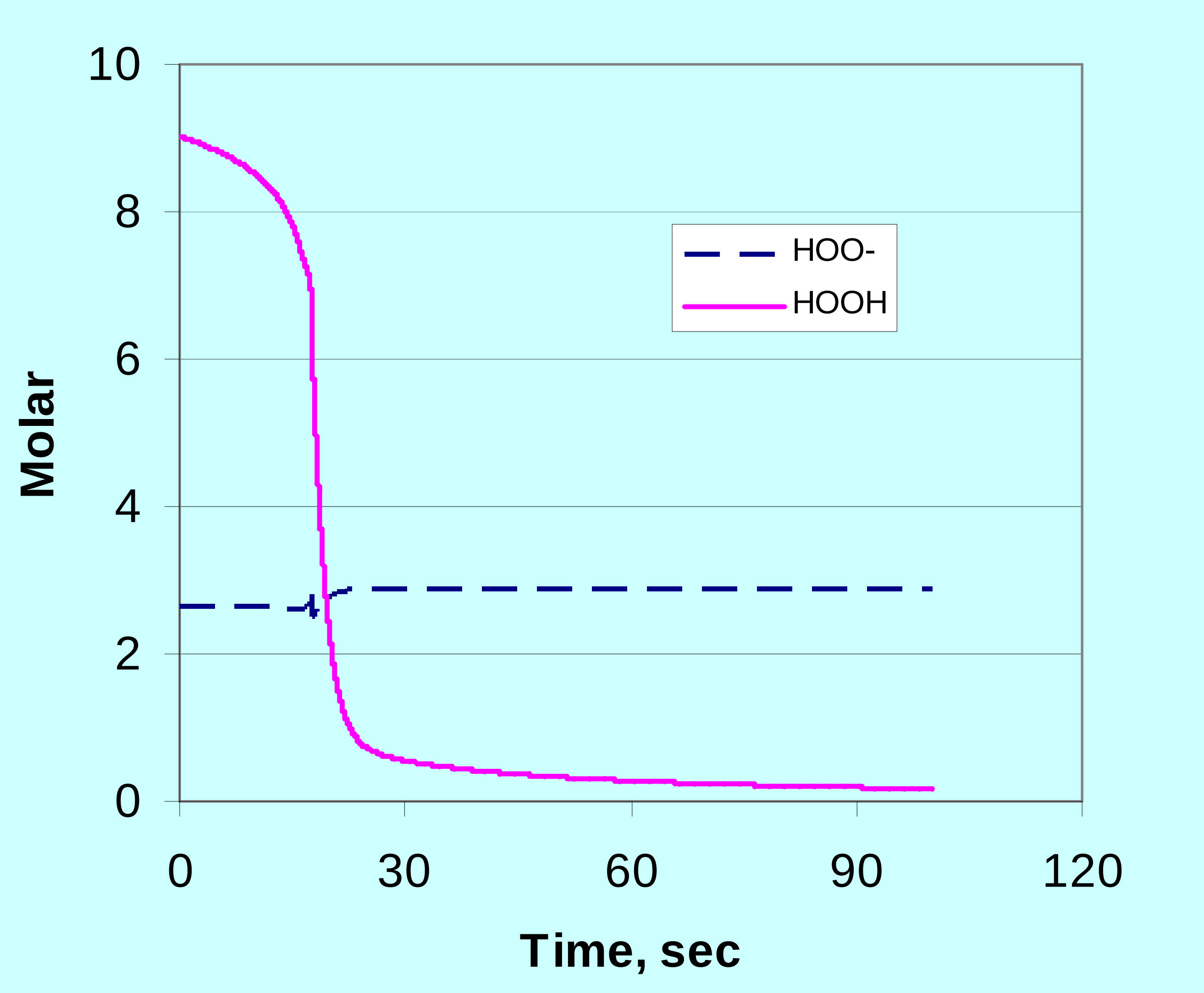
# Peroxide concentration



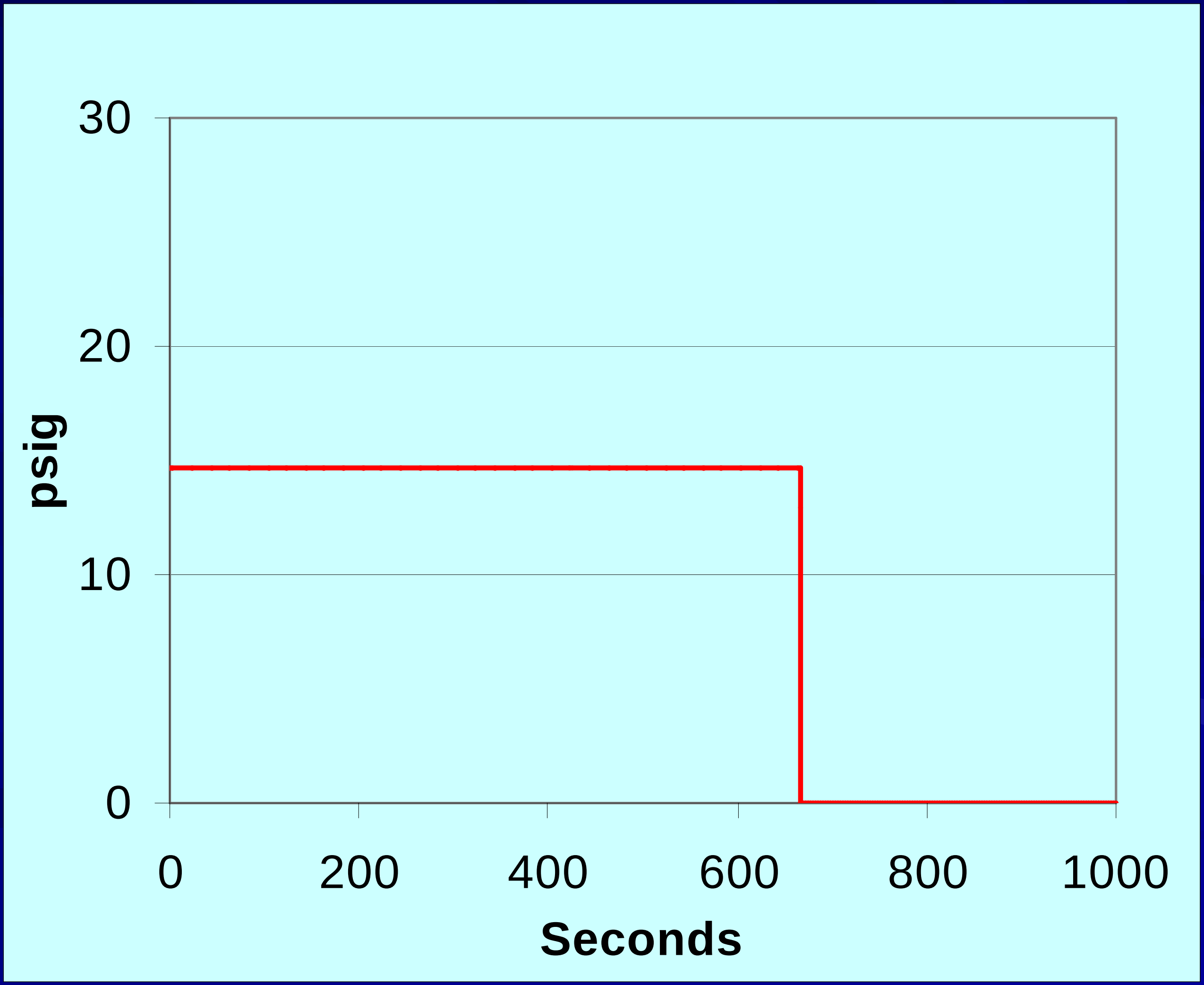
# Without preloaded peroxide



# Peroxide concentration



# 10% peroxide with head start



# Case study

- Canfor Prince George mill.
- D1 tower ruptured and the bleach plant did an emergency shut down.
- 15 minutes later there was a violent explosion of the peroxide stage MC pump.
  - Damage to pump, piping and $D_0$ and $D_1$ towers.
  - Two people injured.

# Canfor incident

- Discharge valve from MC pump was closed but the pump was left running.
- MC can (stand pipe) was plugged with alkaline stock.
- Vacuum assist pulled 50% peroxide into the pump.
- Several high pressure alarms were missed.

# Canfor: Prince George.
MC pump before the accident.

# After!

# The MC pump stand pipe

# The pump impeller

# Evadale incident

- Peroxide stage was an upflow tower.
- An MC pump was used to mix 50% peroxide and caustic.
- Stock flow interlock was to the $D_0$ stage.
- The incident happened on start up after an 8 hour shutdown. Pulp in the dropleg feeding the pump dewatered and bridged, preventing flow into the pump.
- The MC pump exploded, shattering the casing and connected piping.
- The peroxide tower ruptured and extensive damage was caused to the surrounding area.
- Two people were injured.

# What to do

- Peroxide flow must be interlocked to pulp flow measured at the mixer.
- Reduce peroxide concentration – preferably to 10% or less.
- Separate truck/rail unloading stations to reduce risk of accidental mixing of 50% peroxide with other chemicals.
- Do not get complacent – treat 50% peroxide with respect.

# Other issues

- Handling peroxide:
  - Burns
  - Eyes
- Spills
  - Peroxide can start fires (pulp, rags, grease)
  - Peroxide evaporates last

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