PREHEATING CHLORINE DIOXIDE

MIKE BELL, P.E.

PREHEATING CHLORINE DIOXIDE USING BLEACH PLANT FILTRATE OR CHILLER FEED WATER CAN PROVIDE SIGNIFICANT ECONOMICAL ADVANTAGES.

In recent years, competition on a world scale has required that pulp and paper mills run as efficiently as possible. Existing processes are under close review to extract added savings where possible. This article will present a method for saving costs by preheating chlorine dioxide used in the bleach plant.

Chlorine dioxide (ClO_2) solution used by bleach plants is prepared by dissolving gaseous ClO_2 at a concentration of approximately 9 g/L into 40°F chilled water. The solution is stored in chlorine dioxide storage tanks at 40–50°F. The solution is then pumped to the bleach plants and injected into the ClO_2 stages.

A ClO_2 bleach stage normally operates at 160°F. A steam mixer must inject the heat required to raise the ClO_2 solution from 50°F to 160°F into the stock. The steam costs to accomplish this increase in temperature are considerable per year.

Because of the potential savings associated with the reduction of steam costs, the preheating of ClO_2 needs investigation. There are problems and limitations associated with heating the solution, however, due to the unique properties of ClO_2.

PROPERTIES

ClO_2 is an unusual, dangerous, and toxic chemical compound. This very reactive, reddish-yellow gas detonates spontaneously above 5.8 psi partial pressure into chlorine and oxygen without oxygen or air being present. Pure gaseous ClO_2 begins to decompose into chlorine and oxygen at a measurable rate at 85°F. At approximately 120°F, this composition becomes explosive. It is accompanied by a pressure increase of 2–5 times the original pressure depending upon the percentage of ClO_2 concentration. We normally perceive these decompositions as "puffs" in the system.

Although ClO_2 in a gaseous state is dangerous, ClO_2 dissolved in water forms a stable, easily handled solution. This is particularly true when pressurized by a pump at lower temperatures. The ClO_2 exists in solution with water with a vapor pressure of 35–60 mm Hg at 40°F . When an unpressurized ClO_2 solution is heated from 40°F, the solution solubility decreases and the mole fraction of ClO_2 in the vapor state increases. This results in higher vapor pressures. At temperatures exceeding 120°F without pressure, the partial pressure of the gaseous ClO_2 increases to a point where it decomposes spontaneously.

Henry's Law helps to understand a ClO_2 solution. It states that "at any given temperature, the solubility of a gas in a liquid increases with an increase in pressure and is directly proportional to the applied pressure." If we double the pressure exerted on a gas confined above a liquid, the solubility of the gas in the liquid doubles. The pressure furnished by a ClO_2 supply pump therefore provides the driving force to keep the ClO_2 gas in solution even when the temperature increases.

Solutions do not always behave normally upon heating. As a ClO_2 solution is heated, ClO_2 can remain in solution above the expected solubility at the corresponding temperature and therefore become supersaturated. Impurities can then "seed" the supersaturated solution and allow the ClO_2 to evolve from solution unexpectedly. Because of this unpredictability, there can be differences in the behavior of ClO_2 solutions.

SAFETY

Investigation shows that certain safety guidelines are necessary when handling ClO_2:

1. Prevent or minimize any ClO_2 leaks.
2. Limit the maximum ClO_2 solution temperature to 115°F. Many ClO_2 heaters are operating successfully at this temperature. In a particular case with no temperature control, an explosion occurred during the first day of operation due to excessive ClO_2 temperature.
3. Do not shut down ClO_2 supply pumps with hot ClO_2 solution in the lines. Leaking valves can allow the solution to depressurize in the piping system, leaving voids that collect gas that has evolved from solution.

Maximum summer temp.	96°F
Average summer temp. (3 months)	90°F
Average spring and fall temp. (6 months)	72°F
Average winter temp. (3 months)	50°F

I. Mill water temperature conditions

Stage	Water temp., °F, in-out
1st	95-73
2nd	73-57
3rd	57-46
4th	46-38

II. Cooling stages

In summary, ClO_2 is a toxic, potentially unstable, and explosive chemical that requires care in handling—particularly at higher temperatures.

PREHEATING

Over the past few years, mills have used different methods for preheating ClO_2 solutions to accomplish considerable savings. There are two current methods of preheating ClO_2—using bleach plant filtrate and using chiller feed water.

The most common method of preheating ClO_2 solution is to use filtrate from a bleach stage—usually the extraction stage—as the heating medium in a heat exchanger. By preheating the ClO_2 solution from 50°F to 115°F, the mill can realize a substantial savings in steam costs.

Because the filtrate can raise the ClO_2 solution higher than an acceptably safe temperature, the system must include several safety features. The temperature for releasing the ClO_2 solution from the heat exchanger must have close control to keep it within a safe range. To retard and handle any gas formation, the system design must incorporate interlocks that monitor temperature and flow rate.

Certain factors influence the selection and design of the heat exchanger that preheats with bleach plant filtrate. This filtrate usually contains a small amount of fiber that can cause plugging or scaling. The filtrate is usually placed in the side of a heat exchanger that can be cleaned. The side of the heat exchanger handling the ClO_2 solution must have a design to avoid gas pockets. Titanium has proven to be the most corrosion-resistant metal available for ClO_2 service. Three types of filtrate heat exchangers have found use to date: plate type, lamella, and shell and tube. Some companies have found that the plate-type heat exchanger presents leakage problems with gaskets. They have therefore opted for the shell-and-tube type.

Lamella is a flattened-tube heat exchanger marketed in this country for some time. Cases show, however, that at times the metallurgy in these exchangers failed and required replacement by titanium. Although this type of exchanger did not receive blanket approval from the American Society of Mechanical Engineers (ASME) and many were discontinued, several units are operating successfully in this application.

While an installation using bleach plant filtrate to preheat ClO_2 solution provides a good economic return, it has some features that have the potential to create serious problems. These problems apparently stem from inadequate design features. The process might be feasible and acceptable, if one selects a reputable manufacturer who designs the system correctly.

A second alternative for preheating ClO_2 solution is using chiller feed water as a heating medium in the heat exchanger. By using this method of preheating ClO_2, pulp mills can enjoy an excellent return on their investment.

Savings are available in two ways:

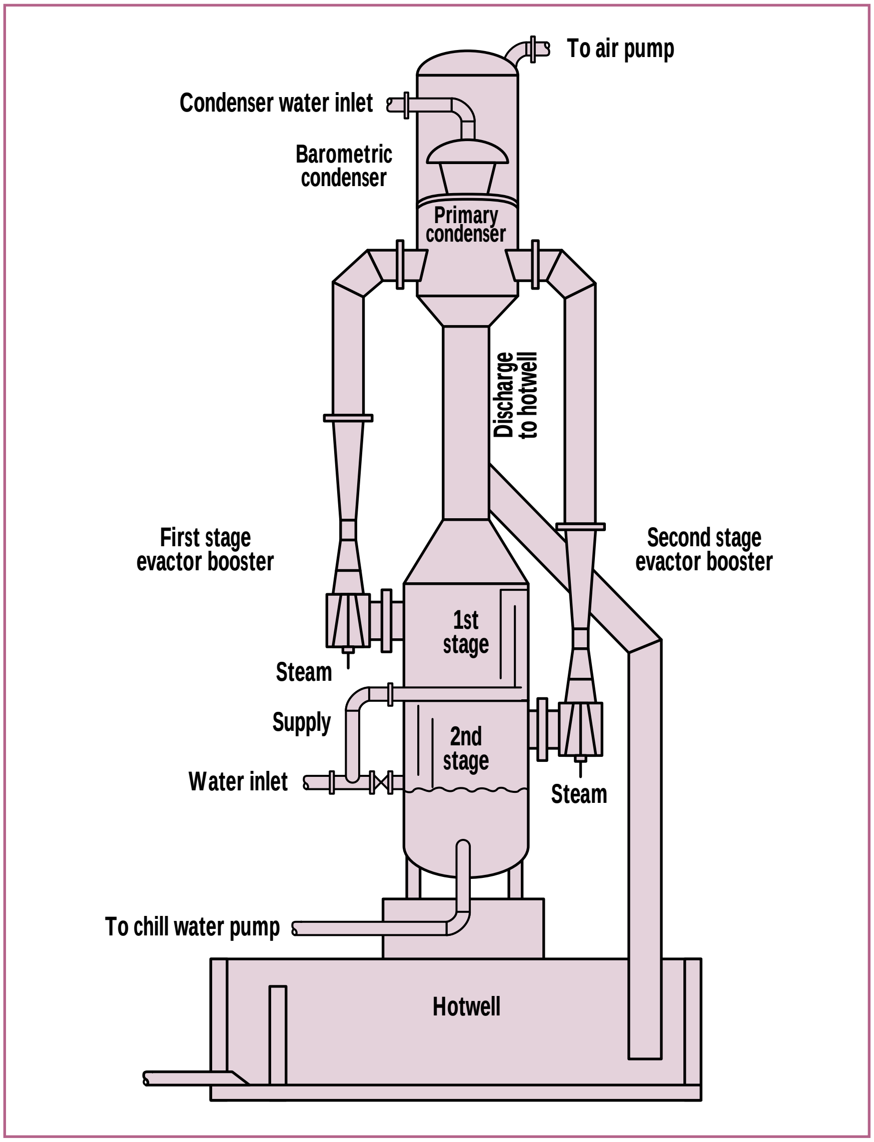
1. ClO_2 solution is preheated and steam is saved at the bleach plant.
2. Chiller feed water is precooled before its introduction to the chiller.

The cooler chiller feed water allows a savings at the chiller. It permits the chill-vactor unit to produce a greater chill water flow rate than the original design. It can also allow one or more stages to be shut down to reduce the steam flow.

The mill water used as the chiller feed water, when supplied from surface water, typically has a winter temperature of 45–55°F and a summer temperature of 90–96°F. Table I shows the typical southern mill temperature conditions normally used for calculations regarding the chiller.

A typical chill-vactor unit takes 95°F mill water and chills it to 38°F. The chill-vactor uses a vertical, multistage chill tank that typically has compartments one above the other. The water flows into the top compartment and then down through the following ones, undergoing cooling in stages. A steam jet connected to each chiller stage pulls a vacuum on its respective compartment. Table II shows how the water cools in each stage.

Since the steam flow to each stage is either operating at 100% flow rate or is shut down, these flows are not



1. Typical chill-vactor unit

modulated. The system normally has controls necessary to automatically shut down a chiller stage and the corresponding steam flow. If the incoming feed water is at 73°F or below, then the controls will shut off the water and steam flow to the first stage so the unit operates with less chiller stages. Equally, if the incoming feed water is 57°F or below, then the second-stage water and its steam flow will shut off (see Fig. 1 showing two stages). Each time a chiller stage and its steam flow are shut down, substantial savings accrue. To provide maximum economic return, the heat exchanger installation must shut down a chiller stage and preheat the ClO_2 solution.

Installing the heat exchanger at the chiller, rather than at the bleach plant, offers many advantages:

1. The capacity of the chiller is increased, or the number of operating stages reduced.
2. The ClO_2 solution reaches a maximum temperature of approximately 90°F in the summer. The lower temperature eliminates most controls and interlocks. The installation is much simpler at the chiller than it would be at the bleach plant.
3. The heat exchanger requirement and metallurgy can be simplified. The chiller heat exchanger can use a stainless-steel shell with a titanium tube bundle, but the bleach plant unit requires all-titanium construction.
4. Installation at the bleach plant requires the purchase of a package unit complete with all the controls from a supplier experienced in ClO_2 systems. The chiller installation operates within a safer ClO_2 operating flow range. One can therefore purchase the heat exchanger from a heat-exchanger fabricator rather than from a ClO_2 system vendor. The purchase is therefore more economical when the heat exchanger is at the chiller.

CONCLUSION

Installing the heat exchanger at the chiller provides a savings in two ways. The ClO_2 solution is preheated, resulting in a savings at the bleach plant. The chiller feed water is also cooled before entry into the chill-vactor. This results in a steam savings and additional capacity at the chiller. TJ

Mike Bell is president, Mar Tech Engineering, Inc., 350 Desiard Plaza Dr., Monroe, LA 71203.