Design considerations for ozone bleaching

A guide to ozone use, generation, and handling

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As ozone bleaching becomes more common, certain engineering design implications must be considered. These include the application of ozone in bleach plants and the generation and handling of ozone gas.

Application of ozone in pulp bleaching

Pulp bleaching with ozone has been researched for several decades by numerous parties around the world. This research has focused on the suitability of ozone as a bleaching agent and the effect of reaction variables, including:

- Pulp consistency
- Ozone charge on pulp
- Ozone concentration in feed gas
- Location of ozone stage in sequence
- Temperature, pressure, and pH.

Low-consistency (0.5–3.0%) bleaching requires ozone gas to be introduced into the pulp suspension and dissolved in the water for reaction. Medium-consistency (5–15%) bleaching requires high-energy mixers, which fluidize the pulp and bring it into intimate contact with the ozone gas. The process with the most laboratory and pilot-plant research is high-consistency bleaching (greater than 20%), which is the focus of our discussion.

High-consistency process

The high-consistency ozone bleaching process is carried out with ozone in gaseous phase, contacting the pulp in a pressurized reactor. **Figure 1** illustrates a typical ozone reactor and associated equipment (*1*). The basic steps of the process are as follows:

1. Acidification of the pulp or pretreatment with viscosity-preserving additives, or both
2. Pressing of the pulp to high consistency
3. Transport of the pulp to the top of the reactor
4. Fluffing of the pulp to separate fibers
5. Passing of ozone-containing carrier gas through the pulp bed
6. Recovery of the carrier gas
7. Dilution and washing of the pulp
8. Recycle treatment of the off gas.

Operating parameters

Ozone charge. Research indicates that the most favorable bleaching reaction occurs at an ozone charge of 1.0–2.0% on o.d. pulp. Increasing the ozone charge above this level decreases the required reaction time, but bleaching effectiveness is reduced, and pulp viscosity and strength may suffer (*2–4*).

Pulp consistency. Studies indicate that ozone consumption and pulp delignification are maximized in the 40% to 55% consistency range (*5–7*). Pulp viscosity remains relatively constant as consistency is increased from 25% to 50% at a given ozone dose, but some pulps suffer viscosity loss at consistencies above 50%.

Ozone concentration. Ozone concentration in feed gas has little effect on pulp kappa number or viscosity, but higher concentrations do tend to decrease reaction times. Additionally, higher concentrations require lower volumes of carrier gas and correspondingly smaller gas-handling equipment.

In summary, the results of research cited in the literature indicate that high-consistency ozone bleaching is optimized at the following conditions:

- Pulp consistency: 40–55%
- Ozone charge: 1.0–2.0% on pulp
- Ozone concentration: 3.0–5.0% in carrier gas.

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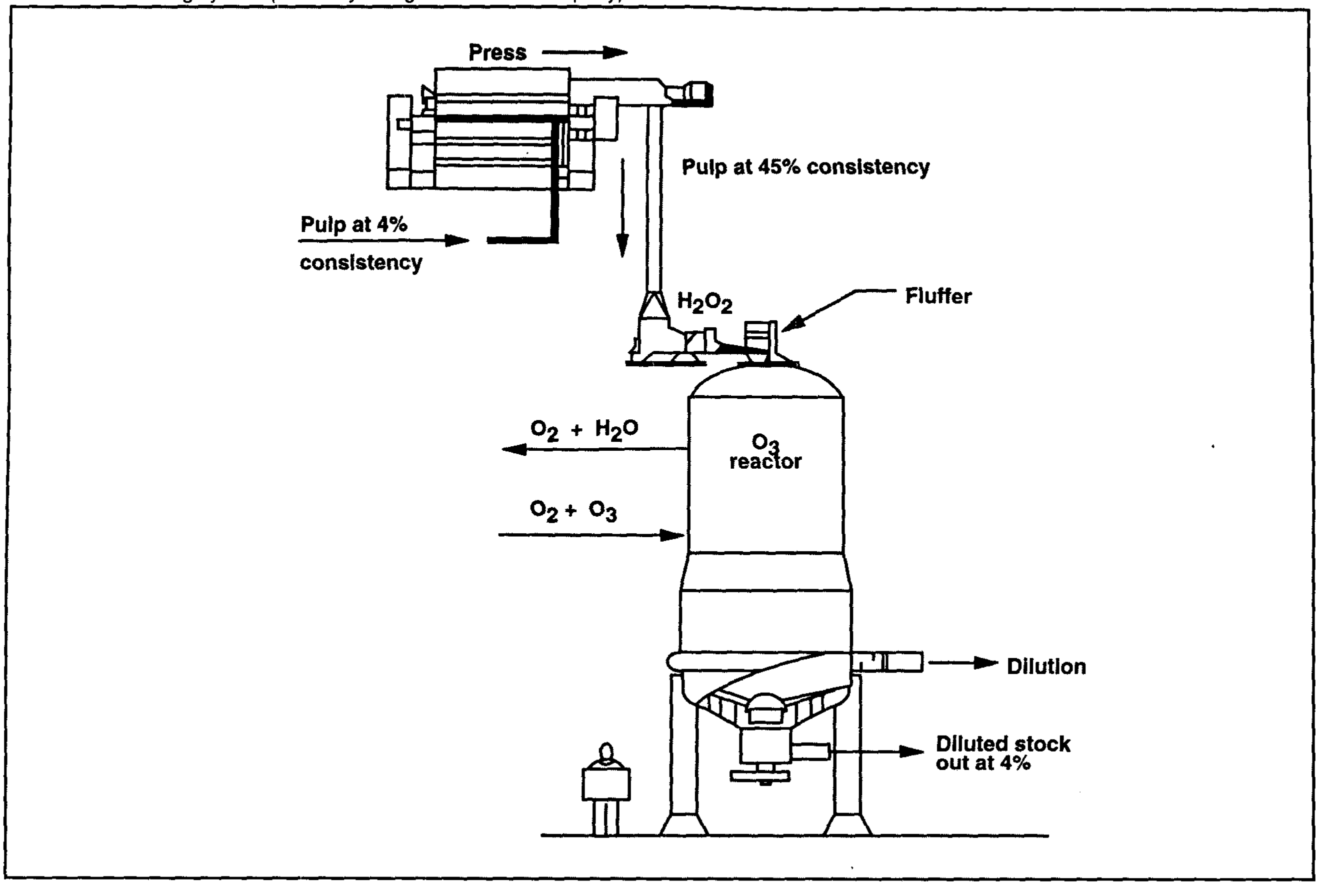
1. Ozone bleaching system (Courtesy of Ingersoll-Rand Company)



Ozone as a bleaching agent

Ozone is an excellent delignifier and brightener of pulp. However, its reactivity is not limited to lignin, and it tends to attack pulp carbohydrates more than conventional bleaching agents like chlorine or chlorine dioxide. Therefore, most research has focused on the use of ozone at the beginning of the bleaching sequence, when extensive delignification is required and the presence of lignin tends to shield the carbohydrates from attack. In this application, ozone is an excellent candidate for replacement of the first chlorination stage of traditional bleach sequences.

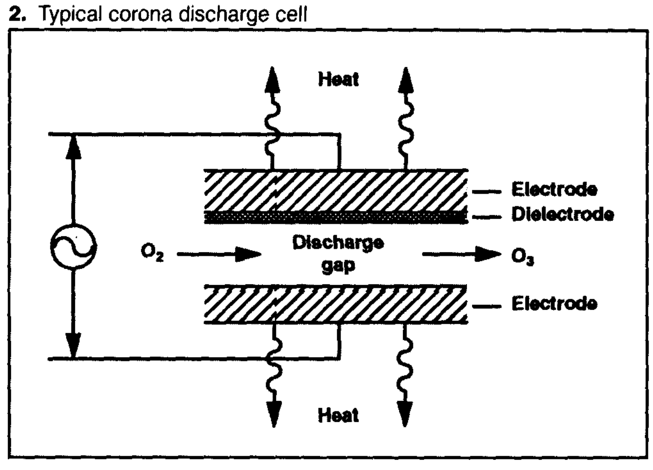
Because application of large amounts of ozone can be harmful to pulp strength, it is often desirable to partially delignify the pulp prior to adding ozone. Oxygen is useful in this role, because it produces effluent that can be recycled and because it already has good acceptance as a pulp delignifier. It has been shown that an O-Z sequence produces superior results to an ozone stage alone (*8–10*).

Environmental impacts

Replacement of chlorine is desirable for several reasons, including:

- Chlorination generates a number of potentially harmful compounds as by-products, which end up in the bleach plant effluent.
- Because of its corrosive nature, effluent from the chlorination stage cannot be recycled to the chemical recovery system and must be treated and returned to the water source.

2. Typical corona discharge cell

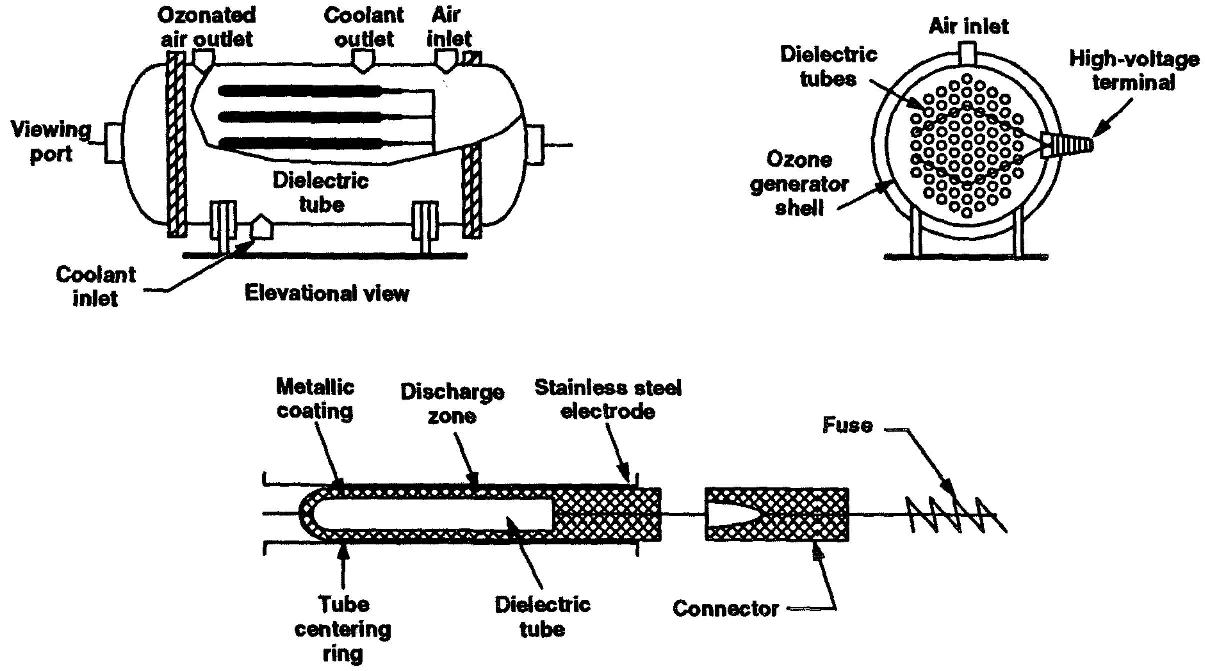


Effluent from an ozone stage can be recycled, which makes a closed (effluent-free) bleach plant possible.

Ozone sequences

Ozone has been studied in combination with many different bleaching agents, both chlorine based and nonchlorine based (*3, 11–19*). In many instances, the bleaching sequences containing ozone were able to produce bleached pulps with brightness and strength properties similar to or superior to conventional bleaching sequences. In all cases, the use of ozone instead of chlorine resulted

3. Horizontal tube ozone generator



in significant reductions of effluent volume, COD, and chlorinated organic content.

Generation and handling of ozone

Generation processes

Ozone, the triatomic form of oxygen, is a powerful oxidizer and a relatively unstable, reactive gas. Therefore, ozone for commercial applications must be generated at its point of use. Small quantities of ozone are generated by several natural and man-made sources such as ultraviolet light, power transmission lines, faulty motor brushes, copying machines, and lightning. Larger-scale generation processes for ozone include corona discharge, ultraviolet radiation, and electrolysis. Because of lower capital cost, ease of control, and lower operating costs, the most widely used process is corona discharge. This process will be the center of the remaining discussion.

Corona discharge process

Figure 2 schematically illustrates a typical corona cell (*20*). Two metal electrodes are separated by a gas-filled gap and a dielectric. Ozone is formed by passing a dry, oxygen-containing gas through the discharge gap while electrical power is applied to the electrodes.

The reaction begins when free electrons in the corona collide with and dissociate oxygen molecules:

$$O_2 + 2e^- \rightarrow 2O^-$$

This dissociated oxygen in turn collides with diatomic oxygen molecules to complete the formation of ozone:

$$2O^- + 2O_2 \rightarrow 2O_3 + 2e^-$$

Competing reactions in the corona lead to some decomposition of ozone:

$$O^- + O_3 \rightarrow 2O_2 + e^-$$

$$e^- + O_3 \rightarrow O_2 + O^-$$

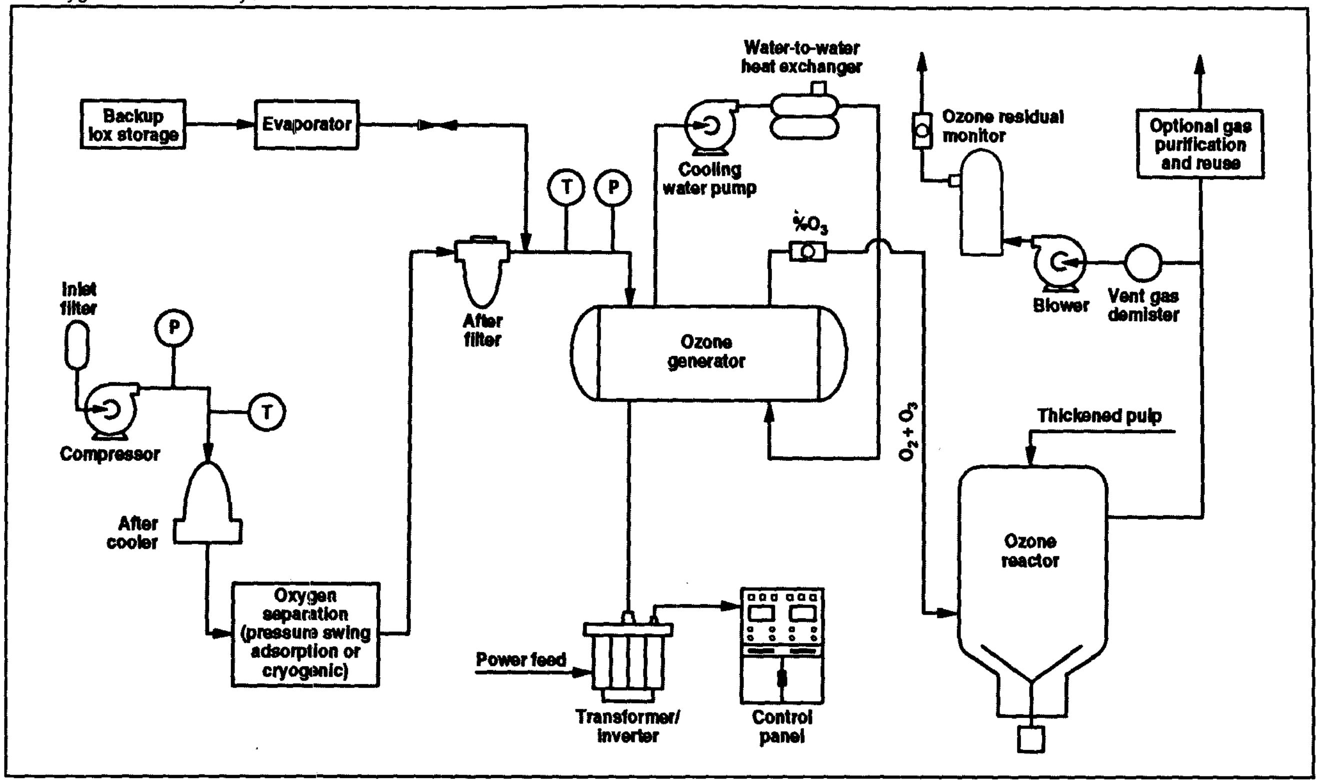
The net ozone yield is the result of all these reactions, and the net ozone production rate is a function of the oxygen content in the feed gas, temperature in the generator, power density in the corona, and ozone concentration in the generator.

System equipment

The heart of an ozone generation system is naturally the ozone generator itself. Generally, numerous dielectric tubes are arranged in horizontal banks inside a shell, as illustrated in **Fig. 3**. The shell has connections for feed gas inlet, ozonated gas outlet, and coolant inlet and outlet. The generation capacities of these units vary, but typically are in the 450 kg/day to 1400 kg/day range. Multiple generators can be arranged in parallel for larger installations.

An oxygen-feed ozone system is illustrated in **Fig. 4**. The major components of this system are feed-gas preparation, cooling, pulp contacting, and vent-gas handling.

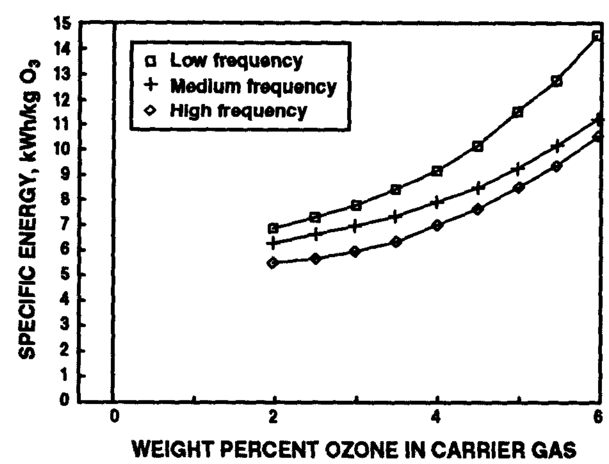
4. Oxygen-feed ozone system



I. Achievable ozone concentrations in carrier gas (%)

	Air feed	Oxygen feed
Low frequency	0.5-1.5	2.0-3.0
Medium frequency	2.5-3.0	5.0-6.0
High frequency	...	9.0

5. Ozone generator power consumption (O_2 feed)



Feed-gas preparation

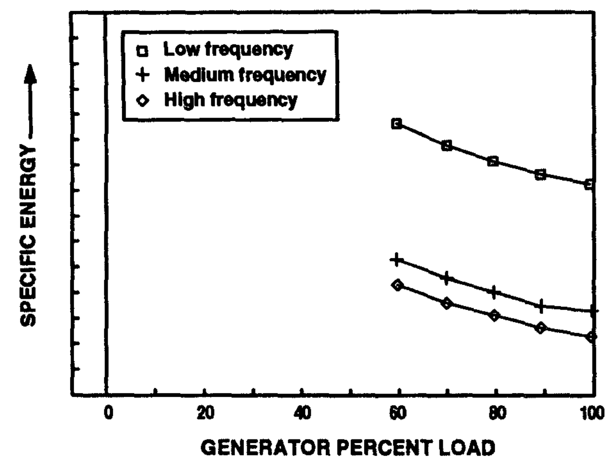
The purpose of the feed-gas preparation system is:

- To provide the ozone generator with the required quantity of oxygen
- To provide this continuous gas supply at the appropriate temperature and pressure
- To limit the quantity of particulates, hydrocarbons, and water in the feed gas.

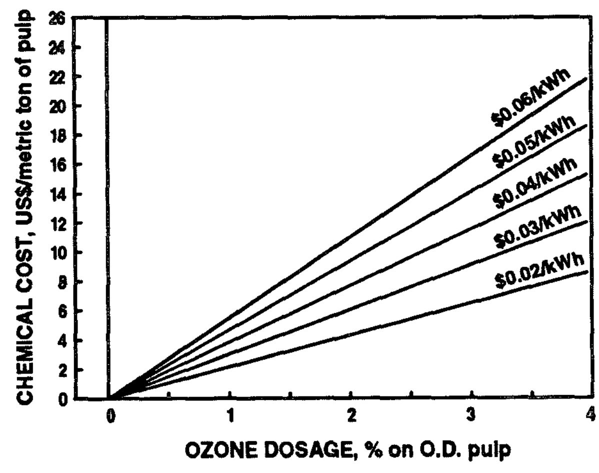
Three feed-gas systems are commonly found at ozone generation facilities: air feed systems, oxygen feed systems, and liquid-oxygen-supplemented air feed systems. The selection of a feed-gas system depends on the type of ozone generator to be installed and the concentration of ozone desired in the product gas.

Air feed systems, although the least costly feed-gas system to install and operate, limit the concentration of ozone in the product to approximately 3.0% by weight. Use of air also requires more ozone generators because of the volume of feed gas required for a given ozone production rate. For this reason, air feed is seldom used in systems with capacities larger than 900 kg/day ozone. Oxygen feed systems, with an oxygen concentration of greater than 90%,

6. Power consumption vs. percent load



7. Ozone cost vs. dosage on pulp



can yield ozone concentrations of 7-8% by weight, depending on generator frequency. Oxygen feed systems can be supplied by cryogenic or pressure swing adsorption systems, or by liquid oxygen. **Table I** presents typical product ozone concentrations for air feed and oxygen feed systems as a function of generator frequency. Liquid-oxygen-supplemented air feed systems are used where ozone demand is variable, such as in a municipal water treatment plant. Liquid oxygen is introduced to boost ozone generation for short-term peak demands.

Because of the ozone volume and concentration requirements for pulp bleaching, the best choice for a feed-gas system is oxygen. Air is compressed and cooled before entering an oxygen separation unit (cryogenic or pressure swing adsorption). Following purification, the 90%+ oxygen stream is filtered to 5-micron particle size to prevent damage to the generator. Water present in the feed gas also can result in damage to the generator by concentrating the corona, leading to dielectric failure. Feed-gas dew points must be maintained at -60°C maximum.

Ozone generator

Ozone quantity and concentration produced by the generator can be controlled by the power applied to the electrodes. Corona discharge generators operate in the 10,000 V to 20,000 V range.

Generators are manufactured for a specific frequency range:

- Low frequency: 50-60 Hz
- Medium frequency: 60-1,000 Hz
- High frequency: >1,000 Hz.

The overall power efficiency of a generator is a function of temperature, feed-gas quality, desired ozone concentration, and operating level versus design level of the generator. **Figure 5** illustrates that as the ozone concentration increases, power consumption increases. Similarly, **Fig. 6** illustrates that low de-rating of a generator results in higher specific energy consumption.

Cooling system

Ozone generation is an inefficient user of electrical energy. Over 90% of the applied power is converted to heat and must be removed by a cooling-water system. Required cooling-water temperature is 15-30°C, resulting in a large quantity of low-grade heat. Cooling-water quality must be maintained at a high level to minimize fouling of the heat transfer surfaces. Most industrial facilities use a cooling tower with treated water to cool their generators.

Vent-gas handling

The vent gas from the ozone pulp reactor contains residual levels of ozone and quantities of hydrocarbons from the bleaching reaction. Traditionally, in water and wastewater treatment facilities, residual ozone in off gas was destructed by thermal decomposition before venting to the atmosphere. However, this practice would result in the loss of expensive oxygen carrier gas in oxygen-feed ozone systems. Current technology allows oxygen-rich off gases to be recycled back to the generator following catalytic decomposition of hydrocarbons to carbon dioxide and water. This water must be removed by a de-mister before reintroduction into the feed-gas stream. A continuous purge of this off gas is required because of gradual enrichment of carbon dioxide and other inert gases in the system. Without a purge, the ozone yield would gradually drop.

Although an improvement over once-through systems, the purification and drying of the recycled off gas is an expensive operation. Some commercial work has been done on a process that separates the ozone from oxygen prior to pulp contacting. Ozone is absorbed on a silica gel inside a vessel, then released by pressure difference when the carrier gas is switched to another vessel. This process allows the oxygen-rich carrier gas to be recycled directly to the ozone reactor (*21*).

Metallurgy and safety considerations

Ozone is a toxic gas and strong oxidant, and it requires safety systems to be installed where ozone is generated. Typically, the construction material of choice is 316 stainless steel for the generator and associated piping. Piping connections are either welded or flanged with fluorocarbon gaskets. Most rubber and plastic gasket materials are not compatible with ozone.

The permissible exposure limit for ozone is 0.1 ppm (volume) for an eight-hour period. Ozone can be detected at 0.01 ppm (volume), and ambient ozone monitors should be located strategically around the facility. Residual ozone monitors often are used at off-gas vents or in oxygen recycle streams to confirm that the residual ozone is being destructed adequately. The relatively low pressures (typically less than 20 psig) of ozone generation and recycle gas streams help minimize the danger of leaks.

Operating parameters and system costs

The largest cost involved in ozone generation is that for electrical power. Specific energy requirements for ozone generation alone (at 4% O_3) are 18-23 kWh/kg O_3 for air feed systems and 7.5-9 kWh/kg O_3 for oxygen feed systems. At a power cost of US$ 0.04/kWh, this converts to chemical costs of approximately US$ 0.82/kg and US$ 0.33/kg for air feed and oxygen feed systems, respectively.

The costs listed above for the oxygen feed system do not include the cost of oxygen itself. The oxygen cost for a given ozone system is a function of the efficiency of the carrier-gas recycle system.

Cooling water also is a variable that must be included in the cost equation. Suppliers of generation equipment often recommend 2500-4000 L/kg O_3, depending on the frequency of the generator. Cooling-water temperature rises are kept at less than 5°C to maintain stable ozone generation. These large cooling-water flows are required to keep gas temperature down and thereby prevent decomposition of ozone (*20*).

Figure 7 illustrates the cumulative cost of ozone, including typical oxygen costs and cooling-water costs. The cost is expressed as cost per ton of bleached pulp at various ozone dosages and power costs.

Summary

We concluded that:

1. Ozone bleaching of pulp is technically viable, based on the research done to date.
2. Optimal ozone bleaching occurs within identifiable ranges of process variables, such as pulp consistency, ozone charge, and ozone concentration.
3. Technology exists today to successfully generate ozone on-site in pulp mills for pulp bleaching.
4. Proper design of peripheral systems such as feed-gas preparation, recycle-gas handling, and cooling water is imperative to achieving successful ozone generation systems.□

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