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Primer for H₂O₂ Environmental Applications

Pollutants in gaseous effluents can be scrubbed with hydrogen peroxide in a conventional scrubber that provides the necessary contact time between the liquid and gas phase. Packed-bed scrubbers are probably the best because their characteristics are known and operating parameters can be calculated. Venturi and spray-chamber scrubbers usually do not provide sufficient contact time.

When biological treatment systems are overloaded and mechanical aerators cannot satisfy the oxygen demand, hydrogen peroxide is often used temporarily to add dissolved oxygen. In such cases, H₂O₂ can be introduced rapidly. Once in the system, it decomposes and releases its oxygen. In certain wastewater, hydrogen peroxide contributes to BOD enhancement, that is, a greater amount of BOD reduction occurs than can be accounted for solely by the oxygen content of the H₂O₂. Nitrogen gas carries sludge particles to the surface of secondary clarifiers. This can be prevented by adding 1-2 ppm of hydrogen peroxide to the clarifiers. Slowing the denitrification process reduces the amount of suspended solids in the effluent. In filamentous bulking, long bacterial strands trap sludge particles and form mats, which cause settling problems in secondary clarifiers. Adding 100 ppm doses of hydrogen peroxide continuously to the return sludge line for five to seven days will usually bring bulking under control.

Usually, a laboratory evaluation of hydrogen peroxide in treating a waste will result in the early optimization of H₂O₂ application at minimum cost. For example, even though the control of phenol with hydrogen peroxide is well established, the presence of catalytic decomposition agents and other reactive substances in the waste stream can influence the amount of hydrogen peroxide needed. When the significant variables – temperature, pH, catalyst concentration and peroxide-to-pollutant ratio are poorly defined (as with mixed organics), these should be analyzed in the laboratory. Plant tests normally should be conducted after a laboratory evaluation. However, such an evaluation is not always useful. In BOD reduction and filamentous bulking control, the most practical approach often is to proceed with a full plant trial, because of the difficulty of simulating biological conditions in the laboratory. Pilot tests should be run when a full-scale unproven test would be costly or the equipment for a full-scale test is not available. For field tests, a drum, tubing and pump setup is enough.

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Injection Methods

Rapid dispersion of hydrogen peroxide into the waste stream is critical, because catalytic decomposition agents are presenting almost every waste stream and these compete with the pollutant in the reaction with hydrogen peroxide. The reaction rate between hydrogen peroxide and the pollutant will usually dictate the point where the H₂O₂ should be added. An addition point 15 to 30 minutes upstream of the control point should be chosen. If this is not practical, because of poor mixing conditions or other physical limitations, compromise addition point should be found and the variables (such as peroxide injection rate, catalyst and temperature) adjusted. In some cases, the addition of a holding tank might even become necessary to increase the reaction residence time.

For wastewater applications, a 50% hydrogen peroxide solution is normally used and is recommended. Lower concentrations, such as 35%, offer no significant safety advantage and carry a cost penalty in freight charges for additional water. Higher strengths, such as 70%, should be avoided because this grade can form detonable mixtures with a wide range of organics. When choosing an injection method, consider the amount of hydrogen peroxide to be used, the precision needed, equipment costs and setup time.

The simplest, cheapest and fastest method is the gravity-feed system. To set it up, attach a plastic spigot to a drum, lay the drum on its side (preferably on a drum rack) and feed by gravity. This system is recommended when flowrate precision is not critical. A rotameter will improve flow control. Pump-feed systems are most precise and require less attention. A low-cost system for permanent service or field trials consists of a drum, polyethylene tubing, polyvinyl chloride fittings and a plastic pump. A more durable system requiring less maintenance consists of drums or an aluminum storage tank, aluminum or stainless-steel transfer and injection lines, and a high quality pump.

Most industrial applications call for 35 to 50% concentration of hydrogen peroxide, in which form it is shipped in drums and tank wagons. To most bulk users, however, it is shipped as a 70%-by-weight solution and diluted at the storage point.

Storage Safety

Although safer than most oxidants if normal safety precautions are observed, hydrogen peroxide is, however, subject to vigorous decomposition by various organic compounds, heavy metals, dirt, heat and alkali storage and handling systems are, of course, designed to minimize such contamination.

Stabilizers are added to hydrogen peroxide to inhibit catalytic decomposition caused by metals and other impurities that might contaminate it during shipment, storage or handling. However, this inhibition is limited. Gross contamination will result in decomposition despite the stabilizers. Hydrogen peroxide's stability is also sensitive to pH. Alkaline solutions are generally less stable than acid ones. For this reason, the chemical is usually shipped and stored as a slightly acid solution. Temperature is also a factor in stability. The decomposition rate increases approximately 2.2 times for each 10°C rise from 20 to 100°C (1.5 times for each 10°F rise from 8 to 212°F). Low temperature has little effect unless substantially below 0°C. Decomposition produces heat, as well as water and oxygen. In dilute solutions, the heat can be readily absorbed by the water. In concentrated solutions, the heat raises the temperature of the solution and accelerates decomposition.

Because freezing points are low and boiling points are high for hydrogen peroxide solutions (-52* and 114°C, respectively, for a 50% concentration), storage tanks can usually be located outdoors in both cold and hot climates.

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Storage must be in accordance with National Fire Prevention Code 43A. Under this code, a 70% solution is listed as a Class 3 oxidizer, and solutions between 27.5 and 52% as Class 2 oxidizers. Fires are unlikely from spills of less than 35% solutions, but can follow if such a spill is allowed to dry on combustible material.

To ensure hydrogen peroxide purity, storage must be restricted to original containers, or tanks of compatible materials, properly designed and thoroughly passivated. Once removed from the original container, hydrogen peroxide should not be returned to it. Tanks must be vented and located away from sources of direct heat. Shipping drums must always be stored head up, preferably on a concrete floor in a cool, clean ventilated fireproof area having a source of water for washing away spills.

Materials of Construction

A high-purity aluminum alloy-specifically, AL 5254, a 99.6% alloy is recommended for bulk storage systems. Aluminum alloys such as 1060 are used for transfer piping, and Type 316 stainless steel for transfer pumps. Iron, steel, copper, brass, nickel and chromium are not recommended for handling concentrated solutions of H₂O₂. Aluminum pipe should be Van Stone flanged, and welded. Screwed fittings should be kept to a minimum. Schedule 80 pipe should be used if threads are to be cut. Teflon tape is suggested for sealing screwed fittings. Valves are generally of aluminum alloy 356 but may be of 300 series stainless steel or porcelain under certain conditions. Preferred valves are ball-type with internal relief seals. However, valves of other designs, made of compatible materials, may be used under certain conditions. If diaphragm valves are used, Kel F or Teflon diaphragms are preferred. As a rule, any valve that could trap hydrogen peroxide must be vented in some manner to prevent pressure buildup in the valve body while the valve is closed.

Centrifugal pumps of aluminum alloy 356 or 300 series stainless steel are recommended for most installations. Mechanical seals may be of glass-filled Teflon, ceramic, or 300 series stainless steel. Other types of packing should be Teflon, never graphite, bronze, copper, lead or common packing materials. Gaskets of Koroseal 700, Kel F and Teflon are satisfactory.

Flexible steel hoses for unloading or transferring should be of 300 series stainless steel. All equipment for storing and handling hydrogen peroxide solutions must be thoroughly cleaned and passivated before being placed in service. Contaminants left behind or embedded in the surface of the storage container could cause decomposition. Gross contamination could result in the rupturing of storage tanks and other equipment.

Aluminum and stainless steels should be passivated as follows: (1) preliminary detergent wash to remove all oil, grease and loose contaminants; (2) trichloroethylene rinse; (3) thorough rinse with clean water, followed by draining to remove the contaminated washing medium; (4) exposure of all parts to an acid solution (preferably nitric); and (5) another thorough rinsing with clean water, followed by draining to remove all acid and water-soluble contaminants.

The size and type of facility will generally determine the specific passivating procedure. In some cases, tanks, pipes and other equipment may be passivated separately before they are installed. IN other cases, it may be necessary to passivate after installation.

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Transportation Modes

Hydrogen peroxide is shipped in drums, tank wagons and tank cars. Standard-size drum containers come in 15, 30 and 55-gal sizes. These are polyethylene, polyethylene-lined fiber, or steel overpack drums. Drum rockers, bung wrenches, valves and pouring spouts are available. Tank wagons with a shipping capacity of 4,000 gal are used for delivery to customer-owned bulk storage tanks. These meet MC 312 specifications, and can carry 70% solutions for dilution on delivery, or 50% and 35% solutions. Most tank wagons are equipped with pump, hoses and fittings for attachment to storage systems. Shipment to large consumers can be by dedicated aluminum tank cars, which range in capacity from 4,000 to 20,000 gal. They conform to AAR specifications for delivering up to 70% solutions. Most cars have an expansion dome with an inspection manhole, a combination safety vent with filtered compressed-air connection, and an unloading connection. Unloading and dilution are usually performed by the customer.

Safety considerations

Although hydrogen peroxide and its decomposition products are not systemic poisons, contact can cause irritation. Concentrated vapors irritate the mucous membranes and the eyes. Eye contact with hydrogen peroxide is particularly dangerous because corneal burns occur very rapidly. If the eyes should be contacted, they should be flushed thoroughly with water. Also consult a physician immediately. Safety glasses or, preferably, goggles should always be worn when handling concentrated solutions.

In addition to eye protection, rubber gloves and suitable protective clothing (such as aprons or coveralls made of polyester acrylic fiber, polyvinyl chloride, polyethylene or neoprene) should be worn. Protective clothing that is not fire-resistant must be washed thoroughly with water after contact. If the hydrogen peroxide is allowed to dry on the fabric, a fire could result, particularly if the clothing is soiled.

Moderate concentrations will cause whitening of the skin and a stinging sensation. This whitening is due to the formation of gas bubbles in the epidermal layer. In most cases, the stinging subsides quickly after thorough washing. High concentrations can cause blistering if left on the skin for any length of time. Such blistering should be treated as if it were a burn. Inhaled vapors can cause irritation and inflammation of the respiratory tract. According to the American Conference of Government Industrial Hygienists, a threshold limit value of 1 ppm (1.4 mg/m³) of hydrogen peroxide vapor in air has been determined as a maximum exposure limit for any 8 hour work day during a normal 40 hour work week. If vapors are inhaled, fresh air should be sought at once; if inhalation has been prolonged, a physician should be consulted immediately.

A mild disinfectant, hydrogen peroxide is useful in counteracting various microorganisms. Because of this antiseptic action, dilute hydrogen peroxide solutions are frequently used to treat open wounds and as a gargle or mouthwash. However, the contact of concentrated solutions (above 3%) with the membranes of the mouth should be avoided. Under no circumstances should hydrogen peroxide be taken internally. If it is swallowed, water should be drunk immediately to dilute it, and a physician contacted. Do not attempt to cause vomiting.

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