

microcrystalline structure. The large number of pores in these materials results in extremely high surface areas (e.g. more than a square kilometer per kilogram, or 0.2 square mile per pound, of solid in some instances). Adsorbents in large-scale commercial use include carbons, silicates, aluminas, and aluminosilicates (molecular sieves).

Generally, adsorption is reversible: The effective adsorption capacity (performance) of a sorbent for a particular solute increases with the concentration of the solute in the gas stream and decreases with increasing temperature. This means that the sorbent may be repeatedly 'regenerated'; that is to say, the solute can be desorbed by passing a lower-concentration or higher-temperature gas stream over the bed. Reversible adsorption is desired for VOC removal because it allows for reuse of the adsorbent. However, in some situations, the adsorption of a solute from a gas is irreversible. The capacity of a solid sorbent is nearly constant and independent of the gas stream composition, but because the solute is so tightly bonded to the sorbent, it cannot be reused.

Activated carbon is the preferred adsorbent material for removing VOCs from gas streams. It has a high affinity for nonpolar compounds, with an even greater capacity for high-molecular-weight materials. The high-molecular-weight compounds can pose some problems, as they tend to be irreversibly adsorbed and effectively decrease the capacity of the carbon in a reversible system. A further problem is that high-molecular-weight compounds can displace lower molecular-weight materials already adsorbed.

The performance of a particular type of activated carbon for a particular solute species must be determined from equilibrium behaviour. Where only one species of solute is present in the gas stream, the equilibrium behaviour is conveniently represented by a simple curve that plots solute concentration in the solid phase as a function of solute concentration in the gas phase. These curves are usually only valid at a single temperature and are known as isotherms. Isotherms for common organic vapours being adsorbed on activated carbon are available in the open literature and from carbon suppliers. They may represent strictly experimental data or, more commonly, experimental data fitted to established algebraic formulas (e.g. Langmuir or Freundlich isotherms). In some rare cases, they may represent purely theoretical calculations of equilibrium based on the molecular statistics of the solute-surface interactions.

Application to VOC removal from gas streams

In designing a carbon adsorption pollution control device in which the inlet VOC concentration is known and a certain outlet concentration is desired, it is possible to determine from the isotherm and material balance calculations how much carbon will be required. The process design is finalised by applying experience factors in terms of 'ageing' of the carbon beds (i.e. loss of capacity with time as a result of pore plugging or some other problem) and safety factors. The desired outlet concentration of the solute in the gas phase is used to determine the concentration of the solute on the activated carbon. When the entire mass of carbon reaches the 'saturation' level, the solute no longer will be adsorbed from the gas stream to the desired level, and 'breakthrough' is said to have occurred. The carbon then must be either regenerated (in the case of reversible adsorption) or disposed of (in the case of irreversible adsorption).

To allow vent streams or other gas streams containing VOCs to come into contact with the activated carbon, the carbon granules are usually arranged in a fixed-bed arrangement in either a vertical or horizontal cylindrical vessel. Small units are manufactured with the carbon already in place (e.g. a canister) with the intent that the entire unit will be replaced when the capacity limit of the carbon is reached. The supplier may regenerate the unit, or it may be disposed of. Larger units are constructed so that the carbon granules are loaded after installation of the vessel. In these units, the carbon may be periodically regenerated in place, or it can be removed and shipped off to a central location for regeneration on a contract basis.

Vapour containment

Transferring volatile organic liquids from delivery tank trucks and tank cars to storage tanks and from storage tanks to process vessels displaces gas from the headspaces that contain some fraction of VOC vapour. While these intermittent vent streams may be treated by one of the add-on control devices described above vapour containment may in some cases be the preferred option. In this technology, additional piping is provided so that as the liquid is transferred from the supply tank to the receiving tank, the displaced gas and vapour from the receiving tank are returned in a separate line to the supply tank. With a properly designed system, very little gas/vapour escapes into the atmosphere, and VOC emissions are minimised. This concept can be extended to filling reactors from drums by using a drum pump and vapour return line rather than picking up the drum and pouring.

Other unit operations that can be improved in terms of vapour containment are those designed to operate at atmospheric pressure. Because of the relatively unrestricted mixing of the process vapours with the atmosphere, reactor and condenser vents open to the atmosphere are difficult-to-control sources of emissions. An option is to operate them as closed systems, at a slight pressure or vacuum, so that the flow of non-condensable gas (air or inert gas) is restricted. This approach is likely to decrease emissions, and the restricted flow rate stream that occurs is easier to control.

Bulk quantities of volatile organic liquids typically are stored in atmospheric pressure tanks with vents to relieve excessive pressure and to break any vacuum that may form. However, diurnal temperature fluctuations will result in 'breathing losses' where the headspace vapour, approximately saturated with volatile organic vapours, is expelled when the temperature rises. When the temperature drops, fresh air (or an inert blanketing gas) is drawn into the tank, from which it may later be expelled with some degree of saturation. Installing 'conservation vents' raises, by a small amount, the pressure or vacuum threshold at which this event occurs, thereby reducing the emission stream volume. Isolated, especially high-pressure, rises or unusually low vacuums will still open the conservation vents, but normal daily fluctuation will not, so that the total volume vented to the atmosphere is substantially reduced.

Process design considerations

To use add-on controls, including vapour containment, a certain amount of process design must be undertaken. However, in the case of new products or revamps of existing processes, it may be possible to use a different pollution control concept—designing a process that has an inherently lower potential for air emissions. One strategy is to minimise the use of VOCs, to substitute lower-volatility (and/or less toxic) compounds, and to keep these compounds contained.

For example, in the case of drying emissions in pharmaceutical manufacture, a modified process design could use and transfer intermediates as solutions or slurries, rather than as dry products. Where solvents are required, a lower-vapour-pressure solvent would tend to minimise evaporative losses and increase recovery efficiency when using condensers. With some processes, a reaction or formulation step traditionally conducted in a solvent possibly could be carried out in an aqueous medium. One ultimate goal may be the practice of a 'solventless' synthesis, where the reaction is conducted 'neat'. In this case, a customised reactor design may be required to handle potential heat transfer and rheological problems associated with the resulting more concentrated reaction mixture.

Although there are often physical or chemical reasons why a process design must incorporate a particular volatile compound, there are many other instances where, with ingenuity, VOC emissions can be minimised by eliminating the offending material altogether.

Another strategy in a modified process design is to minimise the transfer of materials from process vessels by having a particular unit perform more than one unit operation. An example is a filter-dryer

combination. These units, increasingly being used in the pharmaceutical industry, are batch pressure filters that, instead of discharging a wet filter cake, remain closed and convectively dry the cake with a recirculating gas stream.

For maximum effectiveness with some add-on controls, process redesign may be required. An example is the use of closed-loop drying systems.

Acknowledging that a convective dryer is potentially a large source of emissions, a condenser, or a condenser combined with gas compression, is often a good choice. Instead of venting the drying gas, a further refinement of this approach is to recirculate the gas from the discharge of the condenser through the heater and back to the dryer. During the drying cycle there are, other than fugitives, essentially no emissions from the closed loop.

Operational practices

This last control concept deals with the potential for changing workplace practices in such a way as to minimise emissions. Much of the everyday operation of a pharmaceutical synthesis facility is governed by standard operating procedures (SOPs). With proper engineering and management review, the SOPs can sometimes be revised and modified to reduce emissions. One area where emission reductions are particularly possible is in the use of solvents in cleanup practices. Typical procedures may call for the filling and subsequent emptying and air drying of process vessels. The air-drying step results in significant emissions regardless of the vapour pressure of the solvent involved. As an improved SOP, it may be feasible to eliminate the drying step, leaving residual solvent present before the start of the next cycle. Alternatively, a low-VOC aqueous cleaner might be substituted.

A similar emission source involves flushing and blowing transfer lines (piping). Again, it may be possible to change the SOPs so that the lines are left filled with solvent rather than blown dry to the atmosphere.

MINIMAL NATIONAL STANDARDS (MINAS)

Objective

The Minimal National Standards (MINAS) are developed based on achievability and environmental requirements. The objective is to make a general approach for minimisation of pollution and good water quality management by achievable technology. General standards are prescribed irrespective of products and processes of manufacture.

Location specific standards may be prescribed by State Boards taking into account the characteristics of recipient system. The following compulsory and optional standards are stipulated:

<i>Compulsory parameters</i>	<i>Limiting concentration in mg/l except pH</i>
pH	5.5–9.0
Oil and grease	10
Total suspended solids	100
Bio-chemical oxygen demand (5 days at 20°C)	30
Bio-assay test	90 per cent survival after 96 hours. Test should be carried out with suitable species of fish at 100 per cent effluent concentration

<i>Optional parameters</i>	<i>Limiting concentration (in mg/l)</i>
Mercury	0.01
Arsenic	0.2
Chromium (hexavalent)	0.1
Lead	0.1
Cyanide	0.1
Phenolics (as C ₆ H ₅ OH)	1.0
Sulphides (as S)	2.0
Phosphate (as P)	5.0

Notes

1. The optional parameters are applicable to pharmaceutical manufacturing units depending upon the process and products. Formulators are exempted from the optional parameters.
2. State Boards may prescribe limit for chemical oxygen demand correlated with BOD limit.
3. State Board may prescribe limit for total dissolved solids depending upon uses of recipient water body.
4. Limits should be complied with at the terminal of the treatment unit before letting out of the boundary limit.
5. For the compliance of limits, analysis should be done in the composit sample collected every hour for a period of 8 hours.

Environmental requirements vary from one site to another. It is not possible to develop uniform environmentally acceptable standards for the whole country especially in case of waste-water discharge. The receiving body is most important to decide such standards. The concerned regulatory agency can modify the MINAS depending on the local conditions. While prescribing such standards, the following factors are to be noted:

1. Degree of dilution available in receiving system.
2. Protection of important biotic species.
3. Mean tolerance limit for pollutants to the identified biotic
4. Application factors in respect of mean tolerance limit.

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