

Absorption ; Gas absorption ; Gas washing

Introduction Gas absorption is a unit operation by which a gas mixture is contacted with a liquid for the purposes of preferentially dissolving one or more components from the gas in the liquid and to provide a solution of these in the liquid. The very basis of the process is that every gas is soluble in liquid but very-very differently, depending on the gas component to be removed and the liquid. There are many-many application possibilities. For example:

- to produce different acid solutions (e.g. hydrogen chloride, sulphur-dioxide, carbon-dioxide, nitrogen-dioxide etc. is dissolved in water);
- to protect the atmosphere (biosphere) (some pollutant is removed from the gas phase using appropriate solvent for the pollutant);
- to remove solute from the gas phase and/or to recover solute (valuable solvent carried by a gas stream may be recovered for reuse by washing the gas with an appropriate solvent for the vapour).

To do that **mass transfer** is required between the two phases, mass transfer from the gas phase to the liquid phase. During mass transfer the molecules are transferred from the gas phase into the liquid phase through the interface between the two phases. This process is called **absorption**. When the mass transfer takes place in the opposite direction that is from the liquid to the gas phase the process is called **desorption** (or stripping). The principle of both absorption and desorption are basically the same, and we may study both operations at the same time.

The **notation** used are as follows: the equipment is the **absorber**, the operation is called absorption, the liquid (the **solvent**) is the **absorbent** and the dissolved substance is the absorptive.

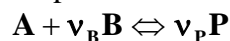
We focus on the environmental protection when some pollutant is removed from an effluent gas (generally air) stream. The gas stream is the processed fluid, hence, its inlet conditions (flow rate, composition including the inlet concentration of the pollutant, temperature and total pressure) is usually known. The outlet concentration of the pollutant is specified by some regulations. Consequently the task of the equipment is exactly specified. The next step of the design procedure is the selection of the solvent. When the solvent is selected its temperature and the inlet composition are generally known.

Solvent selection The choice of a particular solvent is most important. If the purpose is to produce a specific solution, the solvent is specified by the nature of the product (e.g. in the manufacture of any acid solution the solvent is water). If the principal purpose is to solve environmental problems, some choice is frequently possible. In these cases liquids with high solubilities for the solute (for the pollutant) are preferred as a high solubility reduces the amount of the solvent to be circulated. Frequently water is, of course, the cheapest and most plentiful solvent, but the following properties are important for considerations: **Gas solubility:** Solubility shows how much gas can be solved in a liquid thus its measure is e.g. kg of dissolved gas in one kg of solvent (instead of mass fraction mole fraction is also used). The gas solubility should be as high as possible, thus increasing the rate of absorption and decreasing the quantity of solvent required to solve a given problem and also decreasing the operational costs. Generally, solvents of a chemical nature similar to that of the solute to be absorbed will provide good solubility. Thus hydrocarbon oils, and not water, are used to remove benzene from coke-oven gas. The natural components of the air (oxygen and nitrogen) have much less solubility than the pollutants and this gives means for solving the air pollution control. **Volatility:** The solvent should have a low vapour pressure since the gas leaving the

absorption unit is ordinarily saturated with the solvent and therefore much may be lost by using solvent of high volatility. Solvent loss may be costly and may present environmental contamination problems. **Viscosity:** Low viscosity is preferred for reasons of rapid absorption rates, improving flooding characteristics in the towers, low pressure drops on pumping, and good heat-transfer characteristics (if necessary). **Miscellaneous:** The solvent if possible should be non-toxic, non-flammable and chemically stable and should have a low freezing point (the equipment are generally operated outside the buildings). To sum up: the solvent should have high gas solubility, should be relatively non-volatile, inexpensive, non-corrosive, chemically stable, non-viscous, non-foaming, and preferably non-flammable. Generally low-cost solvents should be chosen over more expensive ones of higher solubility or lower volatility. Water is generally used for gases fairly soluble in water, oils for light hydrocarbons, and special chemical solvents for acid gases.

Two types of absorption can be distinguished namely the physical absorption and the chemical absorption. In **physical absorption** only the physical dissolution of the gas is carried out and the dissolved gas is present in the solvent as tiny gas bubbles as e.g. the solution of the carbon-dioxide in water. Physical absorption will never be able to reduce the pollutant concentration very close to zero (or to zero), but it is often desirable. Such conditions can be only met by chemical absorption. In **chemical absorption** a reagent is present in the liquid phase and a chemical reaction takes place within the liquid phase between the reagent and the dissolved gas (the absorptive). If there is enough reagent in the liquid phase the pollutant concentration may be reduced very close to zero (or practically to zero). For practical applications this type of chemical absorption is the most advantageous, since for environmental protection the concentrations of the pollutants are generally very low and hence, chemical absorption is of great importance in the field of air pollution control. Chemical reaction of solvent with the solute will frequently result in very high gas solubility, but if the solvent is to be recovered for reuse, the reaction must be reversible. For example, hydrogen sulphide may be removed from gas mixture using (mono- or di-) ethanolamine solutions since the sulphide is readily absorbed at low temperatures and easily stripped at high temperatures. Caustic soda (NaOH) absorbs hydrogen sulphide or calcium hydroxide (Ca(OH)₂) absorbs sulphur dioxide excellently but will not release it in a stripping operation. Sometimes a reversible chemical reaction will result in a very high solubility and a minimum solvent rate. Data on actual systems are desirable when chemical reactions are involved. **Table 1** on page #5/6 among the figures shows a selection of the suitable absorbent for several pollutants.

Chemical Equilibrium Condition In a chemical absorption process the pollutant A is transferred from the gas phase to the liquid phase where a chemical reaction takes place. It means that the pollutant A and reactant B produce a new compound as follows:



where ν_k is stoichiometric coefficient for the components and the arrow indicates forward and backward (a reversible) reactions. The rate of the chemical reaction is:

$$r = k_1 c_A c_B^{\nu_B} - k_2 c_P^{\nu_P}$$

where k_1 and k_2 is the rate constant for the forward and the backward reactions and c_k is the mole concentration of the components (kmol/m³). In chemical equilibrium the rate of the reaction is equal to zero and the chemical equilibrium constant is defined as follows:

$$K = \frac{k_1}{k_2} = \frac{c_P^{\nu_P}}{c_A c_B^{\nu_B}}$$

For the chemical absorption process it is of great advantage when the chemical conversion is product oriented, that is: the forward reaction is much faster than the backward. This will be the case for high values of k_1 and K . In this case the reaction is very fast and proceeds in the liquid phase very close to the interface. For practical applications this type of chemical absorption is the most advantageous as written above.

Equipment for absorption The purpose of the absorbers is to provide intimate contact of the two phases in order to permit inter-phase diffusion of the constituents. The mass transfer rate is directly dependent on the interfacial surface exposed between the phases, and the nature and degree of dispersion of one of the phases in the other one are therefore of prime importance. The equipment may be classified according to whether its principal action is to disperse the gas or the liquid, although sometimes both phases become dispersed. The gas is dispersed in agitated vessel (rarely used as absorbers) and in tray towers. The liquid is dispersed in Venturi scrubbers, in wetted-wall towers, in spray towers, in baffle towers (or shower trays) and in packed towers. Only a very brief discussion of the different towers will be given here. **Tray (or plate) towers** are vertical cylinders in which the liquid and gas are contacted in stepwise fashion on trays or plates. The liquid enters at the top and flows downward by gravity. On the way, it flows across each tray horizontally and through a downcomer (downspout) to the next tray below. Different tray arrangements and the direction of liquid flow on the trays are used. The gas passes upward through the openings in the tray (riser, chimney), and then bubbles through the liquid forming froth, and disengaging from the froth passes on to the next tray above. The overall effect is a multiple countercurrent contact of gas and liquid, although each tray is characterized by a cross flow of the two phases. Each tray of the tower is a stage, since on the tray the fluids are brought into contact, mass transfer occurs, and the phases are separated. The number of trays (or stages) in a column (or tower) is dependent only upon the difficulty of the separation to be carried out and is determined solely from material balances and equilibrium considerations. **Figure 7** on page #3/6 shows a bubble-cap tray tower, **Figure 8** on page #3/6 shows tray arrangements as well as the directions of liquid flow on the trays, and **Figure 9** on page #2/6 shows typical bubble-cap designs. **Packed towers** are vertical cylinders which have been filled with packing or devices of large surface. The liquid is distributed over, and trickles down through the packed bed, thus exposing a large surface to contact the two phases. The adequate initial liquid distribution is very important. Dry packing is completely ineffective for mass transfer between the two phases, and various devices are used for more efficient liquid distribution. Two major types of packings are used, random or regular. Random packing is that which is simply dumped into the tower and allowed to fall at random. Regular packing is carefully stacked in the tower. Both types of packings have advantages and disadvantages from economic standpoint (investment and operational costs). **Figure 10** on page #4/6 shows a random-packed tower and **Figure 11** shows tower packings. The rings can be used in regular form, too. **Other towers:** Those equipment are mentioned here in which the liquid is dispersed into thin films or drops as Venturi scrubbers, wetted-wall towers, spray towers (spray chambers), baffle towers and shower trays. **Spray tower** (spray chamber) is discussed in more details since it has an important application (see later): The liquid is sprayed into the gas stream by means of pressure nozzles which disperse the liquid into a fine spray of droplets. The polluted gas enters at the bottom and leaves at the top of the absorber and passes through a mist separator before emitted into the atmosphere. The efficiency of this absorber greatly depends on the gas distribution and to maintain as even gas distribution along the cross section of the tower as possible special gas distributors are needed. The pressure drop for the gas stream is low however the pumping cost of the liquid is relatively high. Gas and liquid move

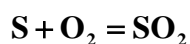
countercurrently in this type of the absorber. The tendency for liquid entrainment by the leaving gas is considerable so an efficient mist (droplet) separator is always necessary. The linear velocity of the gas phase is between from 3 to 5 m/s. The pressure drops of these devices are generally very low.

Absorption plant An absorption plant consists of the absorption unit, the regeneration unit and all necessary auxiliary equipment and machinery. The gas mixture with the gaseous pollutant, namely the solute or the absorptive, enters the absorption unit at the bottom. Within the absorption unit the gas mixture is brought into contact with the liquid (solvent or absorbent). During the contact time the pollutant is at least partly transferred from the gas to the liquid. The purified gas mixture leaves the absorption unit at the top. The liquid normally enters at the top of the absorber and leaves it at the bottom. The liquid leaving the absorption unit and carrying the pollutant is directed to some regeneration unit where the absorbent is treated in such a way that it may be recycled to the absorption unit and the pollutant is disposed appropriately. Regeneration may be achieved by various processes such as vaporisation, rectification, steam stripping, desorption, extraction etc. If necessary, regenerative medium is introduced to extract the pollutant. The solubility of the different gases is decreasing with increasing temperature and decreasing pressure. It follows that the absorption process should be carried out at a relatively low temperature and high pressure. However in air pollution control many times the gas mixture to be treated has a higher temperature and lower pressure. Therefore, the waste gas has to pass through a pre-cooler in order to reduce its temperature as low as possible. A second heat exchanger may be required to cool the solvent after the regeneration to increase the solubility if it is recycled. Another important property which should be observed is the low (sometimes very low) concentration of the pollutant in the gas mixture. In many cases the pollutant concentration is so low that it hardly can be detected in the gas mixture so a very efficient absorption technique is required to remove a tracer component. Sometimes the regeneration is not applied. In this case the used absorbent is generally dangerous waste required further treatment.

Taking into account the considerations mentioned above the absorption unit (absorber) is only one part of the absorption plant which may consist of a regeneration unit, heat exchangers, as well as fans and pumps for transporting the gas and the liquid, respectively. In many cases, the absorption unit is the smallest part of the plant. Earlier the consideration was focused on the absorption process and the absorption unit which is the heart and the most important part of the whole absorption plant. But it should be emphasized that the absorption unit (or the absorber) should be considered in combination with the auxiliary equipment for the optimisation of the process. **Figure 12** on page #5/6 shows the general layout of an absorption plant not showing the fan, pump and heat exchangers if required. An important application of the absorption will be shown in the following.

Sulphur dioxide removal from stack gases.

Sulphur dioxide is an important chemical component of waste gases from power plants when some fossil fuel (coal, crude oil, natural gas) containing sulphur is used as energy source. Before the eighties in Europe (also in the USA) many countries used coal which had high sulphur content (3-4 % m/m). Burning the coal in the boiler the sulphur is also burnt and sulphur dioxide is produced:



If the sulphur dioxide is emitted into the atmosphere it causes the acid rain. Strict international regulation has been applied to decrease the emission of the sulphur dioxide below the emission limit since 1985 (signed by most European countries as well as by the

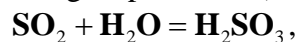
USA, Canada and the UN). At the beginning the requirement was fulfilled by changing the fuel (using coal or crude oil with less sulphur content or natural gas which practically has no sulphur content) but when the regulation was tightening up the desulphurization of the waste gas was introduced. The desulphurization of the waste gas can be carried out with several processes classified into three groups as wet processes, dry processes and half-dry (or half-wet) processes. Mainly a wet process is used all over the world. In this process the absorbent (the solvent) contains calcium hydroxide which reacts with the sulphur dioxide in the liquid phase creating gypsum. **Figure 13** on page #6/6 (and a simple one on page #5/6 where cocurrent flow is used) schematically describes the desulphurization of stack gases.

The volumetric flow rate of these waste gases is of the order of several million m³/h. The polluted gas containing the sulphur dioxide passes through a dust separator (because of the strict regulation generally the electrostatic precipitators or sometimes bag filters are used). The waste gas leaving the dust separator moves to the absorber that may be operated in one or (rarely) two stages (two absorbers connected into series).

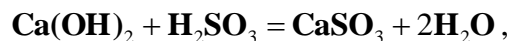
Generally a spray tower is used since the solid material generated during the process can cause a fouling problem using a tray or a packed tower. The liquid is sprayed into the absorber using 2 to 3 bars and the diameter of the drops is between 2 to 3 mms. These conditions give a sufficiently large surface between the phases and the drop entrainment is not too large as well as the energy demand for spraying is also acceptable. The gas velocity in the tower is between 3-5 m/s and the height of the tower may be as high as 20 to 25 ms and the diameter of the tower is generally between 2 and 5 ms. Generally simple steel is used to manufacture the equipment but sometimes some coating is used (stainless steel, rubber, some polymer as PVC, PE, PP, but special alloys also may be used e.g. some Hastelloy alloys, containing 40-60 % Ni, 16-20 % Cr and 2-4 % W in m/m).

The sulphur dioxide is absorbed in the absorbent, where reacts with the calcium hydroxide producing calcium sulphite. The problem is that the calcium sulphite is soluble in water and can not be disposed since the rainwater will wash it into the soil and underground water. It means that an oxidation process is required to get calcium sulphate (gypsum). The steps are as follow:

- absorption in the water, producing sulphuretted (or sulphurous) acid:



- chemical reaction in the liquid phase with the calcium hydroxide, producing calcium sulphite:



- oxidation of the calcium sulphite producing calcium sulphate (which is practically insoluble in the water and it is the reason that gypsum is used as building material):



which contains crystal water (not shown in the chemical reaction), removable only with heating. The flue gas generally contains the oxygen necessary to the oxidation as some excess air is used in the boiler, but more excess air or directly oxygen can be introduced into the lower part of the absorber in order to enhance the efficiency of the oxidation.

The desulphurized waste gas from the absorber moves through a mist separator and to a heat exchanger for reheating it to about 110 °C or higher and finally to stack.

Remark: a quick calculation shows that 1 kg of absorbent containing 0.1 kg calcium hydroxide (10 % by mass) can absorb about 0.086 kg sulphur dioxide which is 86000 ppm (in ideal conditions). It is about 24 times higher than received for physical absorption (it was 3593 ppm) depending on the operational circumstances (temperature, pressure etc.).