

Solvent Recovery Handbook

Second edition

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1 Introduction

From the production of life-saving drugs to the manufacture of household rubber gloves, solvents play a vital role in modern society. However, they share one thing in common—all the world's production of solvents eventually ends up by being destroyed or dispersed into the biosphere. There is a negligible accumulation of solvents in long-term artefacts so the annual production of the solvent industry equates closely to the discharge.

Solvents are the source of about 35% of the volatile organic compounds (VOC) entering the atmosphere from the UK. Their contribution to the total is similar in magnitude to all the VOC arising from the fuelling and use of motor vehicles. Since the latter source is being substantially reduced by improvements in cars and in the fuel distribution system, it is not surprising that increased pressure will be brought to bear on solvent users to cut the harm done to the environment by their discharges.

There are several ways of diminishing the quantity of harmful organic solvents escaping or being disposed of deliberately into the air.

- 1 Redesigning products or processes to eliminate the use of organic solvents may be possible. For example, great changes have taken place and are continuing in surface coatings, which are currently by far the largest use of solvents.

The annual consumption of solvent per capita in the UK through the use of paints, adhesives, polishes, pesticides, dry cleaning and other household products and services is of the order of 12 kg. The only realistic way of dealing with domestic solvent emissions, since the recapture of a myriad of small discharges is impractical, is by reformulation. The change from 1,1,1-trichloroethane to water in typists' correction fluid is a good example.

- 2 Recapture and recycling for sites at which economically large amounts of solvents are used is a valid cure to many problems. Existing plants can have equipment retrofitted, although this is seldom as effective as designing solvent handling systems from scratch with, for example, pressurized storage, interlinked vents and dedicated delivery vehicles for very volatile solvents.
- 3 Selection of solvents or solvent mixtures can have a very significant impact on the amount of recycling possible. Often consideration of solvents is left too late in the process design.
- 4 Photochemical ozone creation potential (POCP) measurements can give some guidance to the choice of solvent which cannot be recovered because quantities are too small. Quite surprising differences of POCP may be found with very similar volatility and solvent properties.
- 5 Styrene and similar monomers can be used in surface coatings to act as solvents to reduce viscosity, polymerizing *in situ* when they have fulfilled their solvent duty.
- 6 Burning of used solvents usefully as a fuel for cement manufacture or as support fuel for an incinerator can be justified logically particularly for hydrocarbon-based solvents since they are the cheapest and have high calorific values. When used as a fuel, hydrocarbons are only used once unlike their use as a solvent with subsequent use as a fuel.
- 7 Incineration to waste provides a last resort for environmentally acceptable disposal. Since this has often been necessary for burning used chlorinated solvent residue, the incinerator needs to be equipped with sophisticated scrubbing facilities.

A great increase in the number of solvents available in bulk took place over the three decades 1920

to 1950. Most of the material available, without the help of gas-liquid chromatography until the mid 1950s, was of low quality and after use was dumped in pits and mineshafts or burnt or left to evaporate in ponds. Industrial solvents were thought of as beneficial apart from a few toxicity problems mostly due to poor ventilation. By 1999 it was realized that they must be used with caution and legislation was provided to cover both the worker exposed to solvent vapours and their global effect at high and low atmospheric levels.

Among solvents that once were commonly used and are now almost completely obsolete are benzene, carbon tetrachloride, 1,1,1-trichloroethane, chloroform, carbon disulphide and the CFCs. They were harmful in a number of ways and safer alternatives have been found for all of them, a trend that will certainly continue. One major reason that is likely to lead to changes of solvent in the future is the need to make recovery easier. There are four reasons why solvents can need recovery because they are unusable in their present state:

1 Mixture with air. This usually occurs because the solvent has been used to dissolve a resin or polymer which will be laid down by evaporating the solvent. Recovery from air can pose problems because the solvent may react on a carbon bed adsorber or be hard to recover from the steam used to desorb it.

Replacement solvents for the duty will therefore have similar values of solubility coefficient and of evaporation rate. The former can be achieved by blending two or more solvents together, provided that when evaporation takes place the solute is adequately soluble in the last one to evaporate. To achieve this, an azeotrope may prove very useful. Particularly in the surface coating industry, where dipping or spraying may be involved, viscosity will also be an important factor in any solvent change.

2 Mixture with water. Whether it arises in the solvent-based process or in some part of the recapture of the solvent, it is very common to find that the solvent is contaminated with water. Removal of water is a simple matter in many cases but in others it is so difficult that restoration to a usable purity may prove to be uneconomic.

It should always be borne in mind that the water removed in the course of solvent recovery is likely to have to be discharged as an effluent and its quality is also important.

3 Mixture with a solute. A desired product is often removed by filtration from a reaction mixture. The function of the solvent in this case is to dissolve selectively the impurities (unreacted raw materials and the outcome of unwanted side reactions) in a low-viscosity liquid phase while having a very low solvent power for the product.

The choice of solvent is often small in such a case, but significant improvements in the solvent's chemical stability can sometimes be found by moving up or down a homologous series without sacrificing the selectivity of the solvent system.

A less sophisticated source of contamination by a solute occurs in plant cleaning, where solvent power for any contaminant is of primary importance but where water miscibility, so that cleaning and drying take place in a single operation, is also an important property. Low toxicity is also desirable if draining or blowing out the cleaned equipment is also involved. In this case there is seldom a unique solvent that will fulfil the requirements, and ease of recovery can be an important factor in the choice.

4 Mixtures with other solvents. A multi-stage process such as found typically in the fine chemical and pharmaceutical industries can involve the addition of reagents dissolved in solvents and solvents that are essential to the yields or even the very existence of the desired reaction. No general rule can be laid down for the choice of solvent, but consideration should be given to the problems of solvent recovery at a stage at which process modification is still possible (e.g. before FDA approval).

To achieve the aim of preventing loss of solvents to the biosphere, it is necessary to recapture them after use and then to recover or destroy them in an environmentally acceptable way. It is the objective of this book to consider the ways of processing solvents once they have been recaptured.

Processing has to be aimed at making a usable product at an economic price. The alternative to reuse is destruction so the processing will be 'subsidized' by the cost of destruction.

Probably the most desirable product of solvent recovery is one that can be used in place of purchased new solvent in the process where it was used in the first place. This does not necessarily mean that the recovered solvent meets the same specification as virgin material. The specification of the new solvent has usually been drawn up by a committee formed of representatives of both users and producers, who know what the potential impurities are in a product made by an established process route. The specification has to satisfy all potential users, who are, of course, usually customers. For any given user some specifications are immaterial—low water content for a firm making aqueous emulsions, water-white colour for a manufacturer of black and brown shoe polish, permanganate time for methanol to be used to clear methane hydrate blockages, etc.

Hence the solvent recoverer may well not have to restore the solvent to the same specifications as the virgin material. On the other hand, the used solvent for recovery has passed through a process that was not considered by those who drew up the virgin specification and knew what impurities might be present. A set of new specifications will be required to control the concentration of contaminants that will be harmful to the specific process to which the solvent will be returned.

It is the drawing up of these new specifications that the recoverer, whether he be in-house or not, has a vital role to play. Specifications should always be challenged. The cost, and even the practicability, of meeting a specification that is unnecessarily tight can be very large. All too often the specification asked for by the user is drawn up, in the absence of real knowledge of its importance to the process, by copying the manufacturer's virgin specification. It will be seen that the cost of reaching high purities by fractional distillation rises very steeply in many cases as the degree of purity increases. This is because the activity coefficients of impurities in mixtures tend to increase as their concentrations approach zero. Even when it appears from an initial inspection that the appropriate relative volatility is comfortably high for a separation, this is often no longer true if levels of impurity below, say, 0.5% are called for.

Not only does working to an unnecessarily high specification increase fuel costs, but also the capacity of a given fractionating column may be reduced

several-fold in striving to attain a higher purity than planned for when it was designed.

In making a case on specification matters, the solvent recoverer needs to be able to predict, possibly before samples are available for test, the cost of recovery of a solvent to any required standard, since it is only by so doing that the true economics of, say, reducing water content may be calculated for the whole circuit of production and recovery. This is now possible in most cases. The properties of most binary solvent mixtures are known or can be estimated with reasonable accuracy. More complex mixtures often resolve themselves into binaries in the crucial areas and, for many ternaries, the information is in the literature. It is therefore possible for the solvent recoverer to play a part in the decision-making process rather than be presented with a solvent mixture that is impossible to recover but cannot be altered.

It is a matter of fact that there are few solvents with properties so unique that they cannot be replaced at an early stage in a product development process. It is also true that the properties which the recoverer depends upon for making separations are not those that the solvent user needs for his product. Cooperation at this early stage is important if the cost to industry's efforts to reduce solvent pollution of the environment is to be minimized.

THE BUSINESS PHILOSOPHY AND ECONOMICS OF SOLVENT RECOVERY

I believe that it is important that the commercial solvent recoverers and the people who are involved with in-house recovery in the pharmaceutical, fine chemical and other industries understand each other's positions.

A commercial solvent recoverer can operate in four different modes:

- Mode 1. As a 'secondhand clothes shop' for solvents acquired by the recoverer and cleaned for resale.
- Mode 2. As a 'laundry' for solvents that returns them to their owner after removing contamination.
- Mode 3. As a 'dress hire firm' supplying, say, a cleaning solvent, taking it back after use and returning it into stock for use by someone else.

- Mode 4. As a 'rag merchant' collecting and sorting solvents too contaminated for economic return to solvent use but of use down market, in this case as fuel.

There is no reason why the commercial recoverer cannot operate in all four modes using the same site, storage, refining facilities, personnel, transport and, perhaps most important of all, the same site licence.

Mode 1

To fulfil this role it is necessary to have a source, or preferably several sources, of any particular solvent and to have a market for the recovered solvent. No solvent user wants to supply a recoverer with used solvent and if he can stop doing so he will. Hence the need for several suppliers if possible. The recoverer will have to guarantee total removal of a used solvent stream but cannot be sure of any arisings.

For the cheaper solvents it makes little sense to seek the market among small users of solvent since their cost savings in using recovered rather than new solvent will be small and therefore will not justify any risk they may be taking. The recoverer should be seeking one or two substantial users who will make a worthwhile annual saving in buying at 70% to 80% of the price of virgin solvent.

The analysis of the recovered solvent will not normally be as good as virgin solvent but it should be tailored to meet the customer's needs and should be consistent. To achieve this a large stock of crude, to provide a fly-wheel in the system, is very desirable. The stock will also reassure the potential customer(s) that he may formulate on recovered solvent for a contract period.

It is advisable, once it has been decided to be a long-term supplier of, say, recovered acetone, to devote substantial storage not only to routine arisings of crude but also 'windfall' quantities coming from accidental contaminations or from the emptying of a system when a plant is closed or a solvent is changed. There are also potential markets such as antifreeze and windscreen de-icer which are very seasonal in sales and for which a recoverer's 'large tank' strategy fits very well.

The cost of holding a large stock of used solvent is, unlike the position in most industries, not large.

In the case of the cheaper and more heavily contaminated solvents the recoverer will be paid to take away used material and a large stock of crude will actually improve the recoverer's bank balance. The cost of renting tankage, once a large tank policy has been chosen, does not vary whether the tank is full or empty.

The other benefit that a 'large tank' policy has is that it allows the recoverer to use his refining capacity when it suits him to do so rather than when (in Mode 2 operation) the owner of the solvent may demand its recovery to a schedule.

With the changes currently taking place in the hydrocarbon fuels industry there are a large number of tanks and depots unused and although these may need some changes to make them suitable for solvent storage they do offer an opportunity to the solvent recovery industry.

Relationships with the prime producers of the solvents which are offered for second-hand sale can be very difficult if parcels of 'cheap' material are hawked around the market often weakening the market price out of all proportion to the quantity involved. Since the prime producers are often the source of accidentally contaminated product and of advice on safe working practice (to protect the good name of the solvents they produce) it is important to maintain good contacts and mutual trust with them. The prime producers will often suggest outlets which can take low specification product and can remove parcels of such material from the market.

Since stocks cannot be allowed to build up for ever the solvents dealt with in Mode 1 must be consumed and not merely returned to the recoverer for further recycling. The use of solvents in paints, adhesives, windscreen wash, etc., where consumption arises by evaporation, is due to decline and this is likely to reduce Mode 1 operation.

Mode 2

The 'laundry' operation involves returning to the customer his own solvent after it has been restored to a reusable condition. There is therefore no general pool of solvent and segregation is necessary at every stage of handling and refining. The commercial recoverer has got to provide a better service than the users can provide for themselves on their own site

and this can be for the following reasons:

- 1 Know-how. While a simple batch-wise flash-over distillation from, say, a mother liquor can be done with minimal operating labour (perhaps 0.5 a person on day work) on a small plant provided as a package by a plant supplier, a more difficult separation may need skilled labour on a complex plant. The specialist recoverer may have the right equipment and labour.
- 2 Capital cost. In the early stages of a new process the throughput of solvent may be very much less than the design capacity of the plant. Solvent recovery is typical of the activities that can be contracted out until the equipment required can be justified on a rate of return basis.
- 3 Manning. At the commissioning and build-up phases of a new process both operating and supervisory staff are fully stretched. The employees of the recoverer provide extra help at this stage.
- 4 Safety. Distillation of solvents involves the safe handling of large amounts of vapour that may be toxic, explosive, flammable or strong-smelling. Some plants may not be able to cope with such material satisfactorily and may have difficulty in getting a site licence.
- 5 Equipment. Unless the solvent recoverers keep abreast of the technologies involved in their field they cannot expect to remain in business in the long run. If they keep up with developments they should be able to offer a better technical service as a specialist than in-house operation can.
- 6 Solvent disposal. At the early stages of a solvent-using process it is helpful to use virgin solvent since this eliminates a possible source of problems. Once the process is proven recovered solvent may be introduced and at the same time the required specification can be adjusted. Only at this stage is it possible to be sure that the recovery plant is designed to recover to the specification.
- 7 Economics. Mode 1 operation demands a sales outlet for the recovered solvent. Some solvents, e.g. acetonitrile (ACN), have virtually no market except at the very highest purity and laundering is the only alternative to incineration or burning in a kiln.

The commercial recoverer can often offer a Mode 1 service at the earliest stage, moving on to Mode 2 when the user is ready for it.

To set against the above there are disadvantages that a commercial recoverer faces.

- 1 Cost of transport between user and recoverer.
- 2 The customer loses direct control of the storage and refining. The latter is a major problem if the FDA or a similar body is involved in licensing. Regular inspection by the customer is necessary in any circumstances.
- 3 Working capital. In view of the fact that the contents of a 100 m³ (or larger) stainless steel storage tank is probably more valuable than the tank itself the working capital cost is important. An on-site solvent refining operation will usually be run on a dedicated column and can therefore be run on a minimum solvent inventory. Indeed the recovery operation can be integrated into the production process. The commercial recoverer will want to build up a stock of crude before running a segregated campaign. The owner of the used solvent is always vulnerable to a large loss if the solvent using process has to be abandoned.
- 4 Turn round. Launderers will seldom dedicate one of their columns to a single stream and will want to operate on long campaigns to get the best split between revenue earning and plant cleaning, shut-down and start-up. Much can be done by good design to reduce turnaround time, which includes not only time on the plant but also recalibrating gas-liquid chromatographs and other laboratory equipment. At best it is seldom that the gap between starting a shut-down and being in full production on the next run will be less than 24 h.

Because of the different approaches of the solvent owner wanting a small inventory and frequent short campaigns, and of the recoverer wanting 'efficient' long campaigns, there is a source of friction here if the two parties have not agreed in their initial contract what pattern of operation should be adopted.

A very different sort of 'laundering' arises infrequently when a ship's cargo is contaminated. The most common contaminant is water used either for cleaning a compartment after a previous cargo or from a mistake in handling. Sometimes the amount of contaminant is so small that the whole cargo can be sold to a customer whose requirements are not so strict as the normal sales specification, e.g. water in vinyl acetate used in emulsion paint. In other cases it

is possible to remove water by circulating a shore tank through a molecular sieve or ion exchange bed.

Although such contaminations are rare they can be very lucrative to the solvent recoverer since the cargo can seldom be returned to the original manufacturer and is truly 'distressed'. It can, however, represent the largest single requirement for working capital that a recoverer may face since a typical cargo size is 500 to 1000 metric tonnes (Te).

Mode 3

While for recovered solvents for reuse in the pharmaceutical industry segregated laundering is probably the only option, for less demanding work, typical of the use of solvents for cleaning and degreasing in mechanical engineering, there is the possibility of solvent being owned only temporarily by the user and being returned as necessary to be cleaned.

The use of solvents for cleaning pipelines and tanks, decomposing methane hydrate and similar non-routine cleaning is a good application for recoverers as is the supply and return of mixtures for testing the efficiency of distillation columns.

Provided the user does not irretrievably contaminate the solvent, e.g. by mixing flammable cyclohexane with trichloroethylene, any chlorinated solvent that has been used for degreasing and not lost by evaporation can be recovered. In Sweden the distributors of trichloroethylene are required by law to supply a removal service, in both bulk tankers and drums, which are bulked together and removed by sea for recovery annually.

For chlorinated solvents (difficult to dispose of) and for difficult-to-recover solvents the possibility of the manufacturers, particularly if they have spare capacity as the consumption of solvents continues to decrease, taking back and refining on their own plant used solvents seems increasingly likely.

Mode 4

About 15 years ago the use of cement kilns to destroy in an environmentally satisfactory way used solvents while, at the same time, using their calorific value became established. In the USA solvent recoverers were the natural collecting point to make suitable fuel blends and to incorporate in these blends the residues they had from the refining of the more valuable solvents.

Cement manufacture is very energy intensive and a low cost fuel is attractive, particularly for the older wet process kilns that use much more heat than the dry process plants.

Kilns have a number of positive features:

- Operating temperatures of about 1400 °C, much in excess of the 1000 °C in conventional chemical waste incinerators. Cement clinker, the product of the kiln, does not form at low temperature so there is little fear of the kiln running at too low a temperature.
- Long residence times at those temperatures, about three times longer than incinerators.
- A very alkaline environment allowing *small* amounts of chlorine to be tolerated though chlorine, fluorine, sulphur and nitrogen are undesirable.
- Dust removal equipment as standard.
- Waste solvent fuel allows coal economy up to about 40% of the fuel purchased while at the same time being a cleaner fuel than coal.

There are tough restrictions on the metals that can be accepted in the waste solvent fuel and this demands a high standard of quality control and should also call for careful selection at the design stage of the metals being introduced into a solvent using process. The blended fuel must also have sufficiently high heating value. Fortunately the lowest cost solvents, aromatic and aliphatic hydrocarbons, are the least worth recovery but have the highest calorific value. Water, of course, should be excluded as far as possible.

It clearly makes sense for the commercial solvent recoverer to act as a fuel blender and this has another advantage.

While complex mixtures need to be treated in plants which can clean-up stack gases and thoroughly decompose complex and often unknown residues, a recoverer can often use material that is better in quality, but still below fuel value, in place of gas oil or natural gas. The flash point of such fuels is seldom above ambient temperature and a well designed boiler-firing system is therefore vital but the economics, even if the crude material must be flashed over to get rid of dissolved or suspended solids, can show a pay-off of a few months.

The foregoing describes the types of operation in which a solvent recoverer may be involved and I will try to indicate the factors which influence their economics.

One can expect to achieve, in selling recovered solvent, 70–80% of the virgin solvent price. The cost of recovery, not including transport, will typically lie in the range £150–300/Te so that the cheaper solvents will have a negative value loaded on transport at the solvent user's works.

- 1 Storage. For Mode 1 operation large storage tanks, usually mild steel in the range 200–1000 m³, are needed for the raw material and the product. These can be costed to the stream on a commercial basis since tanks in this size range are commonly rented by tank storage firms. A figure of £2/m³/month would be typical for mild steel.

For Mode 2 operation, where segregation of comparatively small quantities must be looked after and where used solvent is often brought to the recoverer in drums, storage is often provided in stainless steel road tanks or ISO containers. These will hold 20–25 m³, often corresponding to a batch still kettle, and cost about £20/tank/day (£25/m³/month). These have the advantage that they can be moved to the job, thus minimizing the amount of pipeline cleaning required, moved to the weighbridge for the essential stock balancing function and moved to the drumming and de-drumming facility.

No recoverer ever had enough storage either in terms of the number of tanks or in their capacity. It is not unusual to be unable to carry out a job for lack of tankage. It is important therefore to charge fully storage allocated to a stream.

- 2 Distillation. The cost of fuel is usually not large enough to justify a separate cost heading and it would be included in the hourly cost of distillation. Since plants may vary greatly in size, complexity, capital cost, etc. it is difficult to generalize

on the cost to be charged for their use. A figure of £100/h might be used for purposes of illustration for a plant producing 1 Te/h of overheads.

- 3 Plant cleaning. For a continuous fractionation unit of industrial size the 'lost' time between campaigns for plant cleaning, resetting laboratory equipment, optimizing and stabilizing the column conditions and operator training is appreciable and certainly for the early campaigns of a mixture 24 h would not be unusual. For a batch unit returning monthly to a regular laundry job 6 h would be typical.
- 4 Capital investment in stock. Many of the lower cost solvents handled in a Mode 1 way will be taken into stock for a charge and therefore large storage may be a benefit to cash flow. The Mode 2 laundered streams will be financed by their owners rather than by the recoverer and the owner would normally like to minimize the stock circulating within the segregated system. For a valuable solvent such as pyridine, tetrahydrofuran (THF) or *N*-methyl-2-pyrrolidone (NMP) a stock investment of the order of £100 000 would correspond to a monthly 25 Te campaign with enough recovered solvent in the system to guard against breakdowns or other unforeseen circumstances. The disadvantage of a large stock of expensive solvent is that, if the process is abandoned or the process solvent changed, the disposal into the Mode 1 market is, at best, expensive.
- 5 Residue disposal. Whether the recovery operation is for the removal of water from a solvent, removal of residue or separation of two or more solvents there will always be some waste material to get rid of. Mode 4 plays a valuable role in getting rid of the residue or distillate streams at low costs or even small credits to the process. The disposal of the water phase is always a charge to the job and the capability of activated carbon to remove solvents from water is important here. Like transport this is an 'extra' which must be taken into account for each job.

2 Removal of solvents from the gas phase

The technology for removing volatile liquids from gases has its origins in the operations leading to the production of gas from coal. Removal of naphthalene, which tended to block gas distribution pipes in cold weather, and carbon disulphide, which caused corrosion of equipment when burnt, were both desirable in providing customers with a reliable product. Inevitably, in removing these undesirable components of the raw gas, benzene and other aromatic compounds had to be taken out. Both scrubbing with creosote oil and gas oil and adsorption on activated carbon (AC) were used on a large scale for these purposes and helped to provide some of the earliest organic solvents.

It was therefore a natural step to employ these techniques when the use of solvents on a large scale made the recapture of solvents from process effluent air attractive economically. Our present concern with the quality of air is, of course, a much later development but carbon bed adsorption and air scrubbing are still two of the most frequently used methods of removing solvents from air (Fig. 2.1). To them, we can now add the low-temperature

condensation of solvents from air owing to the demand for liquid oxygen and therefore the availability of very large amounts of liquid nitrogen.

To put the requirements of solvent removal from air into perspective, it is useful to compare the purity levels that are required for a variety of purposes. For this comparison, all the concentrations in Table 2.1 have been reduced to parts per million (ppm) on a weight basis.

To give satisfactory air pollution as far as ozone is concerned, photochemical oxidants which include most solvents should not exceed about 0.044 ppm in the atmosphere.

Deciding on which is the best method of removing solvent from air involves considering both the efficiency of removing the solvent and the quality of the removed solvent. Thus, removing a solvent with a very solubility in water, e.g. a hydrocarbon, means that no drying stage will be needed, while to get a really dry acetone calls for a fractionation stage with a powerful column. Cooling to a low temperature on the other hand would not be suitable for recapturing benzene and cyclohexane.

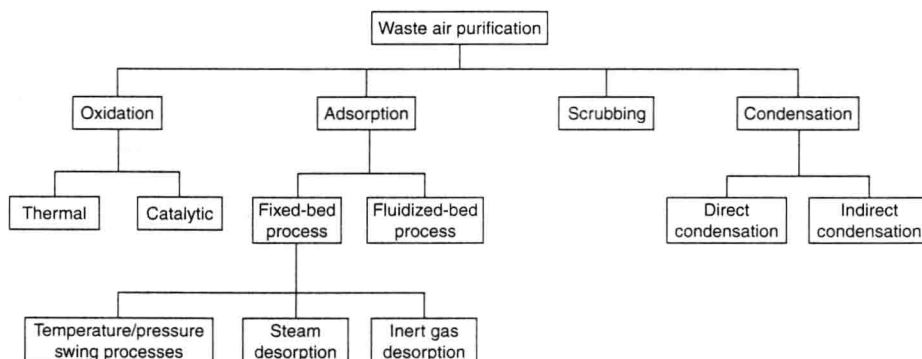


Fig. 2.1 Possible techniques for cleaning up air contaminated with solvent.

While most of the available techniques for waste air purification can be considered, the following should be treated with caution:

- AC with steam regeneration High molecular ketones, alcohols, ethers
- Low temperature condensing Benzene, cyclohexane, dioxane, dimethyl sulphide, cyclohexanol
- Scrubbing Highly volatile solvents
- Bondpore Ethanol, methanol, dichloromethane

SCRUBBING

Scrubbing is a continuous operation and needs comparatively little plot area compared with a conventional AC system. It also has the advantages common to continuous plants in the way of control and the steady requirement of utilities. It lacks, however, the reserve of capacity inherent in an AC bed which, even when close to breakthrough, can absorb large amounts of solvent if a surge of solvent in air reaches it. This is likely to happen from time to time if a batch drier is upstream of the air cleaning equipment, which must be designed to cope with such a peak.

The problems of heat removal inherent in a fixed bed do not arise with absorption. If an air stream

very rich in solvent has to be handled, inter-stage cooling can be fitted on intermediate trays in the absorber column. The restriction of the solvent concentration for safety reasons need not be applied, although flame traps may be fitted in the air ducting. If the pressure drop can be kept low enough, it is possible to position the ventilation fan downstream of the absorber where flammable vapour concentrations should never occur (Fig. 2.2).

The scrubbing column should be operated at as low a temperature as possible. This is because values

Table 2.1 Vapour concentrations

	Acetone	Ethyl acetate	Toluene
Odour threshold	100	1	0.17
TLV-TWA	1000	400	100
IDLH	20 000	10 000	2000
Atmospheric discharge ^a	62	41	26
Air ex drier ^b	7000	1920	3000
LEL	26 000	22 000	12 700
Saturated vapour at 21 °C	250 000	100 000	31 000

TLV-TWA, threshold limit value-time weighted average; IDLH, immediate danger to life and health; LEL, lower explosive limit.

^a TA Luft limit.

^b Typical value usually set to be safely below the LEL.

Table 2.2 Choice of system for removing solvent from air

	Incineration with recuperation	Catalytic incineration	Recovery + incineration	Recovery
Exhaust flow of SLA (cfm)				
30 000–600 000	+	+	+++	+++
30 000–3000	+++	+++	+++	+++
<3000	+++	+++	+	+
Solvent concentration (ppm)				
>15 000	++	+	+	++
7500–15 000	+++	+	+	++
1500–7500	+	++	+	+++
<1500			++	+++
Temperature of SLA (°C)				
>150	+++	++	–	–
60–150	++	++	–	–
<60	+	++	+++	+++

SLA, solvent-laden air.

+++ , very suitable; ++ , suitable; + , rarely suitable; – , avoid if possible.

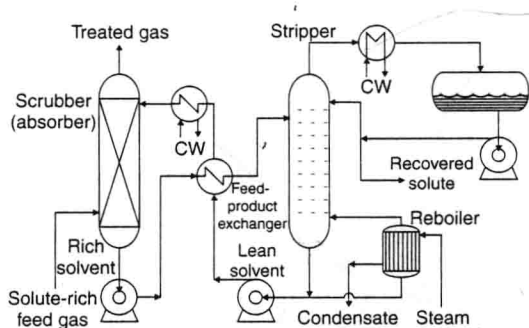


Fig. 2.2 Scrubbing. CW, cooling water.

of the vapour pressure of the pure solvent at the operating temperature (P) are approximately halved for every 17°C fall in temperature. In trying to get the highest possible mole fraction of solvent in absorbent fluid/partial vapour pressure of the solvent (x/p) value this is a modest effect compared with the range of activity coefficient of the solvent in the absorbent (γ) but nonetheless is not to be ignored.

Many of the potential scrubbing liquids become viscous at low temperatures and do not spread well on the column packings which are generally used for absorption. Plate columns can be used but they have a higher pressure drop for the same duty, involving more fan power to move the solvent-laden air (SLA) through the system.

The best clean-up of the SLA that absorption can achieve is for the air to leave the absorption column in equilibrium with the regenerated absorption liquid. This means that the stripping column must remove the solvent to a very low level if some form of back-up (e.g. a small AC unit) does not have to be fitted to prepare the air for final discharge. The possibility of returning the air to the evaporation stage avoids this problem and is theoretically very attractive. The high value of x/p that aided absorption is a handicap to regeneration.

The absorption column handles large amounts of comparatively lean gas and needs to have a large diameter, short column and low pressure drop. In contrast, the stripper has a large liquid load and a comparatively small amount of vapour (the recaptured solvent), tending to lead to a tall column with a small diameter.

Since the stripping column acts through fractional distillation, there is no reason why, by using a mod-

est amount of reflux to fractionate the high boiling absorbent liquid out of the recaptured solvent, it cannot produce a solvent ready for use in many cases.

With good heat exchange between the stripper bottoms and the solvent-rich stripper feed, the heat requirement for absorption is likely to be less than 0.5 kg of steam per kg of recovered solvent. This will depend on the latent heat of the solvent and the amount of reflux required on the stripper. Conventional AC adsorption needs considerably more energy than this.

The scrubbing liquid needs the following characteristics.

- It needs chemical stability since it will be circulated with heating and cooling many times.
- It needs a vapour pressure well above or below that of the solvent being recaptured and no azeotrope with it. If the scrubbing liquid boils below the solvent, comparatively little solvent will need to be evaporated in the stripping column (e.g. methanol stripped from water) while if the solvent is less volatile, the stripping column will need to remove large amounts of water when recapturing dimethylformamide (DMF).
- It needs a low molecular weight so that the solvent will have a low mole fraction in the rich scrubbing liquid.
- It must be miscible with the solvent in all proportions.
- It must not foam in the scrubbing column and must wet the packing well.
- The activity coefficient of the solvent in the scrubbing liquid at low concentration should be low (e.g. <2.0). This disqualifies water for many applications.
- It should be non-toxic, commercially available and economic to use.
- It must not contaminate the treated air too much. To meet TA Luft or 'Guidance Notes' standards a vapour pressure equivalent to a boiling point of about 250°C would be needed for an organic liquid.

Scrubbing depends for its effect on the vapour pressure of the solvent to be recaptured over the absorbent liquor. In the absorption stage, it is desirable to have a high mole fraction in the liquor for a low partial pressure, i.e. a high value of x/p , where

$$\frac{x}{p} = (\gamma P)^{-1}$$

A high value of P corresponds to a highly volatile solvent and indicates that the absorption process is better suited to solvents with a relatively low volatility.

The value of γ is determined by the choice of absorbent and by the concentration of solvent in the absorbent. The latter is usually low and the values of γ^∞ are a good guide in comparing absorbents. As reference to Table 3.8 will show, the values of $\gamma^\infty P$ for water as the absorbent vary over a range of at least seven orders of magnitude. Values of $\gamma^\infty P$ below 500 are worthy of further consideration for water scrubbing recovery. Comparison of water with monoethylene glycol (MEG), however, shows that purely on the grounds of the value of x/p there are possibly better choices for cases where water seems a favoured choice (Table 2.3). For two solutes that have very high values of $\gamma^\infty P$ in Table 3.8 there can, as Table 2.4 shows, be a wide range of performance in other solvents.

There is comparatively little published information on the activity coefficients of volatile solvents in liquids which have high enough boiling points to be considered as absorbents. Nevertheless, the experimental technique of using potential absorbents as the stationary phase in gas-liquid chromatographic

Table 2.3 Comparison of $\gamma^\infty P$ in water and MEG as scrubbing liquids. Lower values are better

Vapour	MEG	Water
THF	3.63	31.15
<i>n</i> -Butanol	6.60	52.3
Methanol	1.07	2.2

Table 2.4 Comparison of $\gamma^\infty P$ for scrubbing benzene and *n*-hexane out of air

	<i>n</i> -Hexane	Benzene
NMP	14.2	1.1
DMSO	64.5	3.33
DMF	17.0	1.4
MEG	430.4	33.9
<i>n</i> -Hexadecane	0.9	1.1
Decahydronaphthalene	1.3	1.5
Water	489 000	1730

columns and eluting the solvent through them is simple and quick.

The vapour pressure of the scrubbing liquid is often the determining factor in its choice because the air discharged after scrubbing is contaminated by it. To meet TA Luft or Guidance Notes standards the scrubbing liquid needs a boiling point of about 250 °C. Diethylene glycol, C14 hydrocarbons and high boiling glycol ethers like polyethylene glycol dibutyl ether are commercially available possible candidates. The hydrocarbon, which would be a narrowly cut mixture rather than a pure chemical, is likely to be the most economical.

The lower boiling phthalates are also worth consideration for scrubbing ethanol and other alcohols from air.

ADSORPTION ON ACTIVATED CARBON

A typical AC system (Fig. 2.3) consists of two beds packed with AC and a valve arrangement to direct the flows. The stream of SLA is directed through the first bed until it is exhausted, or for a predetermined time, at which point it is switched to the second bed. The spent bed is then regenerated, usually with low-pressure steam, and the steam-solvent mixture is condensed. The regenerated bed is then cooled by blowing with atmospheric air before being put back on-stream.

It should be noted that regeneration of gas adsorption AC is very different from liquid-phase adsorption AC. The granular material used in gas-phase operations has a very long life provided that it is

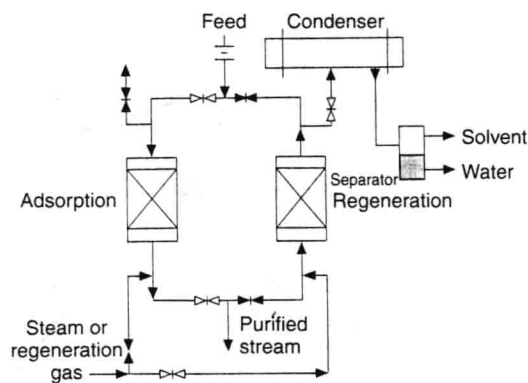


Fig. 2.3 Typical two-bed AC adsorption system.