CLEANING FOR VACUUM SERVICE

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Abstract

This paper will discuss the background to choosing an appropriate cleaning process for a vacuum vessel or component dependent on the pressure regime required. Examples of cleaning techniques and processes will be given and ways of determining whether or not an item is sufficiently clean will be discussed.

1. INTRODUCTION

Experience shows that in order to achieve all but the most modest levels of vacuum it is necessary to clean vacuum vessels and components in some way. This is because as far as vacuum is concerned, the world is a dirty place! In general, vessels and components will have been machined, worked in some way or another, or handled. Such processes may use greases or oils which have high outgassing rates or vapour pressures and which will remain on or in the surface. Marking pens and adhesive tapes leave residues on surfaces which can also enhance outgassing. Water, solvents and other liquids can remain embedded in cracks or pores in a surface and can outgas over long periods. All such contamination can limit the base pressures attainable in a system.

In general terms as far as vacuum is concerned, we define contamination as anything which

- prevents the vacuum system from reaching the desired base pressure

- introduces an unwanted or detrimental species into the residual gas

- modifies the surface properties of all or part of the vacuum system in an undesired way

Thus for example, a pool of liquid mercury in a vacuum system will, at room temperature, limit the base pressure to about 2×10^{-3} mbar, its vapour pressure. If the system were required to operate at, say, 10^{-5} mbar, the mercury would be a contaminant.

In an electron storage ring, the cross section for electrons scattering off a residual gas molecule increases as the square of the atomic number, Z, of the scattering species. Thus, for long beam lifetimes (i.e. low electron losses), it is important to minimise the partial pressures of high-Z species which are contaminants in the residual atmosphere.

In a system operating at 10^{-8} mbar, the partial pressure of hydrocarbons might be 10^{-11} mbar. These hydrocarbon molecules striking a mirror surface can crack or polymerise when irradiated by electrons or photons, leading to maybe graphite-like overlayers or to insulating layers. A complete monolayer might form in about 12 days, assuming that 1 in every 10 molecules impinging on the surface is cracked and sticks. The optical properties of the mirror are therefore altered by the surface becoming contaminated.

Hence there is a necessity to clean to remove actual or potential contaminants. We will define a suitable cleaning process as one which results in the residual vacuum being suitable for the task. This definition is heavily influenced by the observation that most people who use vacuum are not interested in vacuum as such but are interested in an industrial process (semiconductor chip production or metal refining for example) or a scientific experiment (such as studying chemical catalytic reactions on a surface) or operating a machine (maybe a particle accelerator). What they are interested in is having a defined, controlled atmosphere and vacuum is just the simplest way of achieving this.

In this discussion, we shall be considering in very general terms some of the factors influencing the choice of a cleaning process. This article is an overview and does not pretend to be a comprehensive review citing the literature in detail. A (very) short and selective bibliography is given

at the end and interested parties can use the references in these papers as a starting point for a more in depth survey.

2. CHOOSING A CLEANING PROCESS

There is no one cleaning process which is "right" for all vacuum systems, vessels or components. Some of the things which will need to be taken into account are as follows

- the level of vacuum required (rough, high, UHV, etc)
- if there is a particular performance requirement (e.g. low desorption)
- whether there is a particular contaminant (e.g. hydrocarbons) whose partial pressure must be minimised
- what materials the items are made from
- how the items are constructed
- safety
- cost

Once these have been considered, and we will look at some of these in more detail below, then one can begin to choose a cleaning agent and the necessary processes to achieve the desired result.

It is important to realise that there are very many different "recipes" in the literature and in the folklore of vacuum. Advocates of a particular process or procedure will defend their choice with an almost religious fervour. Generally, this is because the procedure "works" for them, i.e. it meets their requirements. Often this procedure will not have been tested rigorously against other possible procedures which might be equally good if not better (in some sense) and will therefore in no way have been optimised. This is not necessarily a problem. It often simply means that the processes being used may not be as economical or convenient as they might be. Whether this is important or not depends on the individual situation.

In this article, we will look briefly at both chemical and physical cleaning processes. There are, however, some general points which should be taken into account when deciding what to use. Some of these are as follows.

- Some "cleaning" processes which are often used are applied more for cosmetic purposes to make vacuum chambers look clean by producing mirror finish surfaces and so on. Whether from a vacuum point of view they are actually cleaner is by no means to be taken for granted. Such surfaces could, for example, exhibit enhanced outgassing.

- The minimum chemical cleaning process compatible with the level of vacuum/cleanliness required should always be chosen. The less that needs to be done to a vacuum surface the better.

- Chemical cleaning is a hazardous procedure so must be done safely!

- Processes such as bead or shot blasting, grinding, scraping and mechanical polishing can leave dirt trapped in voids in the surface of materials which can then be very difficult to remove.

- Acid treatments such as pickling, passivation or electropolishing can trap acids in the surface of the material. For demanding UHV applications, a vacuum bake to 450ºC is required to remove these completely.

3. DEPENDENCE ON THE BASE PRESSURE REQUIRED

In general the lower the base pressure required, the more rigorous the cleaning process will need to be. (Note that in general it is preferable to use the term "base pressure" rather than "ultimate pressure" which is commonly used. Base pressure refers to the lowest normal pressure attained in a vacuum system in its working condition, whereas ultimate pressure strictly refers to the lowest pressure obtained in a standard defined system measured in a standard way.)

Fig 1 illustrates in a very schematic fashion some typical common cleaning processes which would be used in sequence. To use this figure, select the approximate pressure required and then apply all the processes in order from the top to the level corresponding to the pressure required.
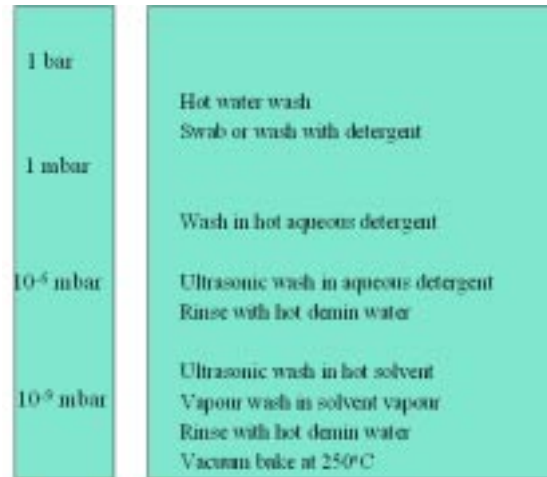

1 bar	Hot water wash
	Swab or wash with detergent
1 mbar	
	Wash in hot aqueous detergent
10^{-6} mbar	Ultrasonic wash in aqueous detergent
	Rinse with hot demin water
	Ultrasonic wash in hot solvent
10^{-9} mbar	Vapour wash in solvent vapour
	Rinse with hot demin water
	Vacuum bake at 250°C

Fig 1: Simple cleaning procedures

4. DEPENDENCE ON CONTAMINANTS

The user will have to determine what level of contaminants can be tolerated in any given process. It is important to distinguish between the total pressure required in the system and the partial pressures of particular species which can be allowed. As has been said, most processes use vacuum simply because it provides an easily controlled environment for the process and it is really what can and cannot be tolerated in that environment which is important.

For any given process, the user may have to determine by tests what cleaning is necessary to obtain the desired environment.

As has been discussed above, one very common requirement is to reduce hydrocarbon contamination to a minimum. This will often best be achieved by washing in a hot organic solvent such as trichloroethylene or perchloroethylene (where use of these substances, both chlorinated hydrocarbons, is permitted) followed by washing in hot clean demineralised water and a vacuum bake.

A general cleaning recipe that works in many circumstances is given in Section 7.1.

5. HOW CONSTRUCTION AFFECTS CLEANING

In order to clean a vacuum component to the highest standards - e.g. capable of working at UHV with very low levels of contaminant species in the residual vacuum - at the design stage careful consideration must be given to how the item is to be cleaned. In particular, crevices, blind holes, cracks, trapped volumes, etc., should be avoided as these will act as dirt and solvent traps. It can be very difficult to remove both dirt and solvent from such areas. Fortunately, good vacuum practice regarding trapped volumes will also result in a component which avoids these problems.

A good design working at lower vacuum levels will also seek to remove any such traps.

One component which must be cleaned with particular care is thin-walled edge-welded bellows often used for motions in vacuum. Care must be taken that the cleaning process does not cause particles to be left in the convolutions, since these can puncture the bellows when it is compressed.. Alkaline degreasers can be particularly prone to this as they often throw precipitates. During cleaning, the bellows should be fully extended and a careful final wash with demineralised water and a blow dry with hot compressed air, both inside and out, must be done.

If the process uses chlorinated hydrocarbon solvents then these must be removed completely by heating, as any left behind can corrode the bellows, leading to leaks. This last point is particularly true for accelerators, where the atmosphere in accelerator tunnels can often be warm and humid. The radiation environment also promotes enhanced corrosion, leading to premature failure of the welds.

6. CHEMICAL CLEANING AGENTS

A chemical cleaning agent is simply any substance that might lead to removal of an unwanted contaminant. They will generally be liquids of some sort and will work either by dissolving or by reacting with the contaminant or by removing the surface layers of the substrate and hence liberating the contaminant.

Care has to be exercised that the cleaning agent itself does not introduce contaminants. This will obviously depend on the end use of the item being cleaned. For example, as noted above, hydrocarbons are often a serious contaminant in a vacuum system. However, in mineral oil sealed mechanical vacuum pumps, e.g. rotary pumps, this is not the case as much of the mechanism is of necessity bathed in hydrocarbons. Therefore a major manufacturer of such pumps uses a hydrocarbon mix to clean the piece parts for his pumps and enjoys the benefit of residual lubrication and corrosion protection on parts not normally lubricated by the pump fluid. In most cases, however, what is desired is an agent that will remove contamination from the item without recontaminating it in some way. The operator has therefore to ensure that the solvent is changed regularly before the build up of contamination in solution becomes a problem. Examples of some typical cleaning agents are shown in Table 1. The table should be read with caution and is to be regarded as a starting point only. In all cases, manufacturers data sheets should be consulted and expert technical advice sought before using agents of this type.

The majority of these agents are solvents, which dissolve the contamination present on a surface. Some rely more on a simple washing action, flushing contaminant off the surface, as in a water jet. Others, e.g. detergents, work mainly by reducing the attractive (Van der Waals) force between contaminant and surface atoms. Some work by chemical action e.g. by etching a thin layer off the surface thus releasing the contaminant. The alkaline degreasers and citric acid work this way, as do, to some extent, some detergents. It is important to understand how any particular agent interacts with the materials to be cleaned in order to avoid unexpected side effects.

It should be carefully noted that, in some countries, some of these substances are either banned or their use is strictly controlled under legislation or regulation. It is therefore imperative that the operator consults the relevant authorities before implementing a process involving these agents.

7. CHEMICAL CLEANING OF SPECIFIC MATERIALS

Clearly, any cleaning process must not damage the component being cleaned. Most accelerator vacuum systems are made from stainless steel or aluminium, and from now on we will concentrate our discussion on matters particularly relevant to accelerators. However, contained within such vacuum systems there may well be copper, titanium, beryllium, ceramics of various sorts, and various other materials. Below we will note some cleaning processes which have proved to be satisfactory for these materials.

It must be emphasised once again, however, that it is very important that the user checks that any particular cleaning agent or process is safe for the materials to be cleaned.

7.1 Stainless Steel

The procedure described below for cleaning stainless steel is a very high specification process for the very demanding requirements of an electron storage ring where cleanliness is of paramount importance. For less demanding applications, the procedure could stop at the appropriate point in the procedure where requirements had been met.

6.1.1   Remove all debris such as swarf by physical means such as blowing out with a high pressure air line, observing normal safety precautions. Remove gross contamination by

Table 1
Some typical cleaning agents

Agent	Examples	Advantages	Disadvantages	Disposal
Water		Cheap; readily available	Need to use demin for cleanliness. Not a strong solvent	To foul drain
Alcohols	Ethanol, methanol, iso-propanol	Relatively cheap; readily available; quite good solvents	Need control – affect workers; some poisonous; some flammable; stringent safety precautions	Evaporate or controlled disposal
Organic solvents	Acetone, ether, benzene	Good solvents, evaporate easily with low residue.	Either highly flammable or carcinogenic	Usually evaporate!
Chlorofluoro-carbons (CFCs)	Freon™ (CFC-113)	Excellent solvents; evaporate easily with low residue	Banned!	Strictly controlled – must not be allowed to evaporate.
Chlorinated hydrocarbons	Methyl chloroform; trichloro-ethylene ("Trike")	Excellent solvents. Non toxic. Low boiling point. Low residue.	Methyl chloroform banned. Trike may be banned. Toxic, require stringent safety precautions	Strictly controlled
Detergents		Aqueous solutions, non toxic. Cheap and readily available. Moderate solvents.	Require careful washing and drying of components. Can leave residues	To foul drain after dilution.
Alkaline degreasers	Almeco™, sodium hydroxide.	Aqueous solutions, non toxic. Moderate solvents	Can leave residues and may throw particulate precipitates.	Requires neutralisation, then dilution to foul drain
Citric Acid	Citrinox™	Cheap and readily available. Quite good solvents.	Require careful washing and drying of components. Can leave residues. Unpleasant smell.	To foul drain after dilution.

washing out, swabbing or rinsing with any general purpose solvent. Scrubbing, wire brushing, grinding, filing or other mechanically abrasive methods may not be used

6.1.2 Wash in a high pressure hot water (approx. 80°C) jet, using a simple mild alkaline detergent. Switch off detergent and continue to rinse thoroughly with water until all visible traces of detergent have been eliminated.

6.1.3 If necessary, remove any scaling or deposited surface films by stripping with alumina or glass beads in a water jet in a slurry blaster.

6.1.4 Wash down with a high pressure hot (approx. 80°C) water jet, with no detergent, ensuring that any residual beads are washed away. Pay particular attention to any trapped areas or crevices.

6.1.5   Dry using an air blower with clean dry air, hot if possible

6.1.6   Immerse completely in an ultrasonically agitated bath of clean hot stabilised trichloroethylene for at least 15 minutes, or until the item has reached the temperature of the bath, whichever is longer.

6.1.7   Vapour wash in trichloroethylene vapour for at least 15 minutes, or until the item has reached the temperature of the hot vapour, whichever is longer.

6.1.8   Ensure that all solvent residues have been drained off, paying particular attention to any trapped areas, blind holes etc.

6.1.9   Wash down with a high pressure hot (approx. 80°C) water jet, using clean demineralised water. Detergent must not be used at this stage.

6.1.10 Immerse in a bath of hot (60°C) alkaline degreaser (P3 Almeco™ P36) with ultrasonic agitation for 5 min. After removal from the bath carry out the next step of the procedure immediately.

6.1.11 Wash down with a high pressure hot (approx. 80°C) water jet, using clean demineralised water. Detergent must not be used at this stage. Ensure that any particulate deposits from the alkaline bath are washed away.

6.1.12 Dry using an air blower with clean dry air, hot if possible.

6.1.13 Allow to cool in a dry, dust free area. Inspect the item for signs of contamination, faulty cleaning or damage.

6.1.14 Vacuum bake to 250°C for 24 hours using an oil free pumping system.

6.1.15 Reduce the temperature to 200°C and carry out an internal glow discharge using a helium/10% oxygen gas mix.

6.1.16 Raise the temperature to 250°C for a further 24 hours then cool to room temperature.

7.2 Aluminium

6.2.1   The CERN specification for aluminium chambers is as follows -

6.2.1.1 Spray with high pressure jets at 60°C with a 2% solution of Almeco 29™ (an alkaline detergent).

6.2.1.2 Repeat with a 2% solution of Amklene D Forte™.

6.2.1.3 Rinse thoroughly with a jet of hot demineralised water.

6.2.1.4 Dry with hot air at 80°C.

6.2.2   Another procedure known to give good results is -

6.2.2.1 Immerse in Sodium Hydroxide (45 gm-1 of solution) at 45°C for 1 - 2 min.

6.2.2.2 Rinse in hot demineralised water.

6.2.2.3 Immerse in an acid bath containing Nitric acid (50% v/v) and Hydrofluoric acid (3% v/v).

6.2.2.4 Rinse in hot demineralised water.

6.2.2.5 Dry in warm air

7.3 Copper

Under most circumstances, copper can be cleaned using the same procedures as for stainless steel. However, it should be noted that some of the proprietary formulations of alkaline degreasers attack

copper and leave surface stains. Organic solvents are usually all right, and cleaners based on citric acid are very good for copper. Indeed, some of these are formulated specifically for this purpose. As always, thorough washing in hot demineralised water and drying in warm, dry air should be undertaken.

Copper is particularly susceptible to surface staining, fingerprints showing up very well! Under some conditions, light surface oxidation tales place which results in a visible blackish film on the surface. As long as this is not a thick, friable or flakey deposit, this will not usually be a problem in vacuum, since it thermally disassociates quite readily.

7.4 Beryllium

Working with beryllium is subject to stringent safety requirements and the appropriate safety authorities must always be consulted before carrying out any such work. However, provided that care is taken to ensure that no particulates are generated and that suitable precautions are taken, components may be handled safely. Impervious gloves should always be worn when handling beryllium and any skin abrasions or cuts should be covered up.

No stripping, cutting, machining or abrasive operations may be carried out on beryllium except in purpose built facilities.

Otherwise, beryllium may be cleaned in accordance with the procedures for stainless steel.

7.5 Titanium

Titanium may be successfully cleaned as for stainless steel.

7.6 Glass

Simple detergents and hot water washing are effective for cleaning glass.

7.7 Ceramics

Alumina powder in a water or an isopropanol carrier may be used to remove surface marks from ceramics such as alumina or beryllia. Baking in air to the highest temperature that the material can stand or to $1000^{\circ}C$, whichever is lower, is very effective for removing contamination from the surface pores of the material.

8. PHYSICAL CLEANING TECHNIQUES

8.1 Blowing

A jet of compressed air or inert gas is a useful technique to remove particulates and liquids, particularly from blind holes, as well as surface dust. A laboratory or site compressed air supply may be used provided that the air supply derives from an oil-free compressor. It should be distributed via cleaned and dried air lines and there should be particulate filtration at or near the point of delivery. Alternatively, bottled gas, e.g. nitrogen, may be used, but again the delivery line should be clean and dry.

8.2 Bead Blasting

A jet of alumina or silica or some other inert material in the form of small beads is directed onto a surface and physically strips material away. The carrier may be either air or water. The latter is gentler, but both techniques carry the risk of driving contaminants (and beads!) into the surface. Some surface damage may occur. However this is a useful technique for stripping, for example, deposited metal films from the inside of vacuum vessels.

8.3 "Snow" Cleaning

This technique uses a jet of pellets of solid Carbon Dioxide which is directed onto the surface. This is a non-impact technique which is good for removing particulates and also apparently some hydrocarbon films. It is however, expensive and noisy.

Unlike bead blasting, the technique does not damage the surfaces being cleaned, since the solid CO_2 does not impact the surface. As the particles, usually in the form of small cylindrical pellets, approach the surface at high speed, the shock wave travelling ahead of the particle is reflected from the surface and interacts with the pellets, which sublime. The cleaning action is effected through a cavitation process in the compressed gas as it reflects from the surface.

8.4 Cutting and Grinding

Cutting and grinding are used to remove surface layers. Both have their place provided they are done with care. Each technique usually requires a lubricant between tool and workpiece, which for vacuum use is best to be either water or water based, although a good alternative is alcohol. If possible dry cutting is best.

There is a danger of driving contaminants, cutting fluids and swarf into the surface where they can remain trapped.

8.5 Polishing

Polishing is a gentle form of grinding and carries the same dangers. However fine hand polishing is often required to remove surface blemishes. A useful material for this is ScotchBrite™ which is essentially fine alumina in a polymeric carrier in the form of a loose weave mat. Diamond powder wetted with alcohol and applied on a lint free pad is also acceptable. Polishing involving pastes and waxes is to be avoided

Small components are often polished in a tumble polisher in which they are immersed in a bath of small wet stones or steel pellets of various shapes which is gently stirred or tumbled.

9. PASSIVATION

As far as cleaning is concerned, passivation techniques are essentially ones which prevent the adsorption of contaminants into the surface of a vacuum system or prevent the permeation of gas from the bulk material into the vacuum system. By and large, these involve the formation of a barrier layer of some sort on the surface.

Some examples are

- oxide films, produced by air baking, glow discharge or other techniques.

- coatings, such as TiN or BN put on the surface by sputtering. These have not been much used except in demonstration systems and will not be discussed further here.

- active films, like getters or NEG. These are discussed in other chapters of these proceedings.

10. SPECIAL CLEANING TECHNIQUES

10.1 Ultrasonic Cleaning

This is essentially a method of enhancing a chemical cleaning process. Fig 2 shows the principles involved.

The figure shows a two stage cleaning plant (Fig 2(a)). The workpiece is first suspended in the hot liquid (darker shade) in the left hand tank. The ultrasonic transducers set up a pattern of ultrasonic waves in the liquid. As these waves reflect off the surface of the workpiece, interference takes place and a series of cavitation bubbles are generated (Fig 2(b)). Collapse of these bubbles results in contamination particles being dragged off the surface. The contamination then either dissolves in the liquid or, if insoluble, eventually drops to the bottom of the tank as sediment. The result is an enhanced cleaning process. As jobs are cleaned, the liquid in the ultrasonic tank gradually becomes more contaminated and eventually some of this remains on the surface of the workpiece, or indeed may be transferred to it from the liquid. To ensure full cleanliness, the workpiece is withdrawn from the liquid and is suspended in the second (right hand) tank in the solvent vapour (lighter shade). This vapour is generated by the boiling liquid solvent at the bottom of the vapour stage tank. The vapour
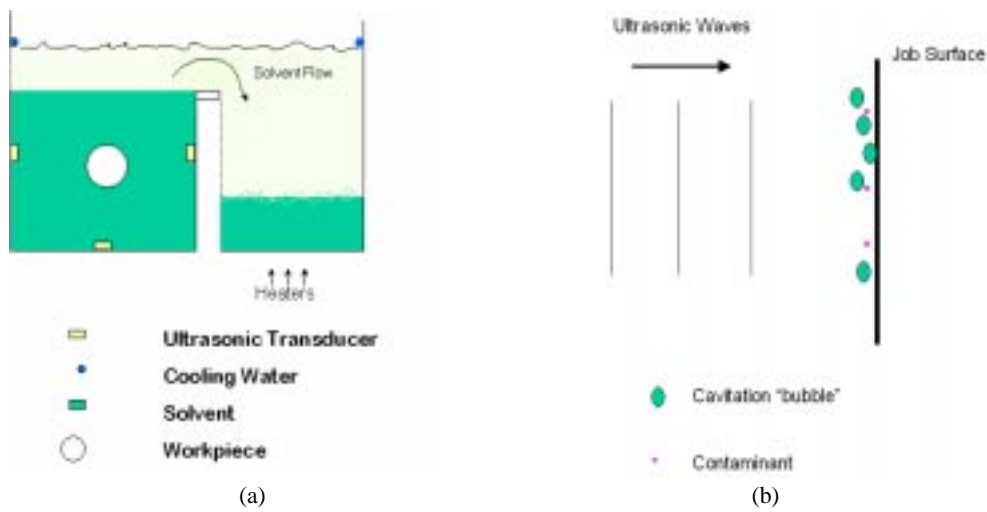
<p style="text-align:center">(a)   (b)</p>

Fig 2: Schematic of ultrasonic cleaning (a) two stage ultrasonic dip/vapour wash tank (b) the cleaning process

condenses on the workpiece so that it is washed in the pure liquid solvent condensate which drops back into the boiling liquid, taking the residual (soluble) contamination with it. At the top of both baths are cooling coils which condense the vapour before it can escape from the open top of the tank. These coils are arranged so that the liquid runs back into the ultrasonic stage. This pure liquid solvent tops up the ultrasonic tank and contaminated solvent flows over the dam into the boiler. Thus a distillation process is set up with the contamination gradually being concentrated in the bottom of the vapour stage and the liquid in the ultrasonic tank remaining relatively pure, hence enhancing the life of the solvent charge.

10.2 Electropolishing

Electropolishing has often been assumed to reduce outgassing by reduction of the surface area presented to a vacuum system. In practice, for any technological metal surface, the real surface area is very much larger (factors of several) than the physical area, because on a macroscopic scale there will be many pits, grooves, cracks, grain boundaries and other defects. Although electropolishing does indeed remove surface asperities and smooths the edges of cracks, the actual benefit achieved is not very great.

However, electropolishing does remove the amorphous surface layer which is formed when polishing a metal surface (the so-called Beilby layer). It replaces this layer with a relatively well ordered surface oxide layer, which may have barrier properties preventing diffusion (particularly of hydrogen) out from the bulk of the metal into the vacuum.
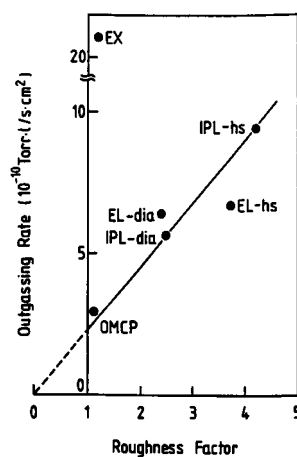

Fig 3: Outgassing rate as a function of surface roughness (taken from Suemitsu *et al*, J Vac Sci Technol **A10**, 1992, 570)

On the other hand, electropolishing may introduce hydrogen and other contaminants into the surface layers in significant quantities. These can subsequently diffuse out and actually increase the outgassing rate over that of the starting material. Electropolished components require a good bake (preferably at $450^{\circ}C$) to thoroughly outgas the surface in order to see any real benefit.

Despite many studies over a long time, it is only in some recent very careful work on aluminium prepared by various techniques that a correlation between surface roughness and outgassing rate has been demonstrated and even in these results there are some anomalies (Fig 3).

10.3 Glow discharge

Glow discharge cleaning is an effective final cleaning process which reduces outgassing and desorption rates. It achieves this essentially by three mechanisms

- The bombardment of a surface by medium energy ions (a few hundred eV) directly desorbs gas adsorbed on the surface and absorbed in the sub-surface region.

- If the discharge gas contains oxygen (or water), oxygen ions (O_2^+ and O^+) are created in the discharge. These can react with the adventitious carbon which is always present on a surface to form CO and CO_2 which can be pumped away. Carbon overlayers, usually graphitic or amorphous in character, seem to act as gas reservoirs on a surface.

- A good, well ordered oxide film is generated on the surface which acts as a diffusion barrier.

For accelerators, it is normal to use a simple dc glow discharge, although an ac (rf) discharge may also be used. Fig 4 shows a typical set-up for dc discharges. A gas is admitted to the vessel to be cleaned and a positive dc potential of a few hundred volts is applied to a rod or wire electrode along the axis of the vessel. If the gas pressure is of the order of a few tenths of a mbar (dependent on the actual gas being used and the precise geometry of the vessel) a discharge will be struck and a visible glow seen. The gas molecules are ionised in this discharge and are accelerated to the grounded walls of the vessel which they strike with moderate energies. It is advantageous to stream the gas along the vessel, admitting it at one end and pumping at the other. At these pressures the flow is viscous and this helps to sweep the desorbed gases from the system.
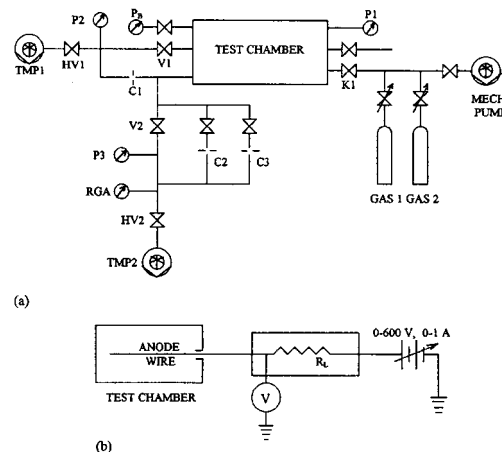

Fig 4: Schematic of glow discharge apparatus (taken from Li and Dylla, J Vac Sci Technol **A13,** 1995, 572)

Various gas mixtures have been used. $Ar/10\%$ O_2 is the traditional mix and is very efficient; pure O_2, pure N_2, pure H_2 and $He/10\%O_2$ have also been used effectively. There are a number of criteria which are used in selecting the gas. Of critical importance is whether sputtering of the metal surface is a problem or not. If there are insulators present, then sputtering can cause conducting films to be deposited over their surfaces if they are exposed to the sputtered atoms. Oxygen in the mix seems to help alleviate this by forming thermally unstable metal oxides which are removed from the surface in the discharge. Lighter species sputter less efficiently and so help obviate the problem. Also, heavier gas ions can become buried in the metal surface and can diffuse out over time. This may or

may not be a problem depending on the application. Carrying out the discharge at elevated temperature (e.g. 200°C) helps minimise such accumulation. Thus the discharge can be conveniently carried out during a bake cycle.

It is helpful to know when to terminate the glow discharge. If, as has been suggested above, the primary benefit is achieved by the removal of adventitious carbon by forming CO and CO_2, then monitoring the concentration of C^{12} in the discharge exhaust gas with a residual gas analyser will give a termination point when this concentration ceases to reduce.

For particle accelerators, this procedure is usually carried out as part of the pre-installation processing programme, since *in situ* glow discharge is difficult in practice.

The benefits of glow discharge cleaning for particle accelerators are by no means fully established. For proton machines fabricated from stainless steel the benefits are well established. For electron machines where the beam space tends to be surrounded by copper, the evidence is not well in place, although it is believed to be beneficial. A definitive experiment is planned for ANKA in the near future.

Fig 5 shows data from two laboratories showing the effect of glow discharge cleaning stainless steel on, respectively, outgassing rates and photodesorption yields.

(a)   (b)
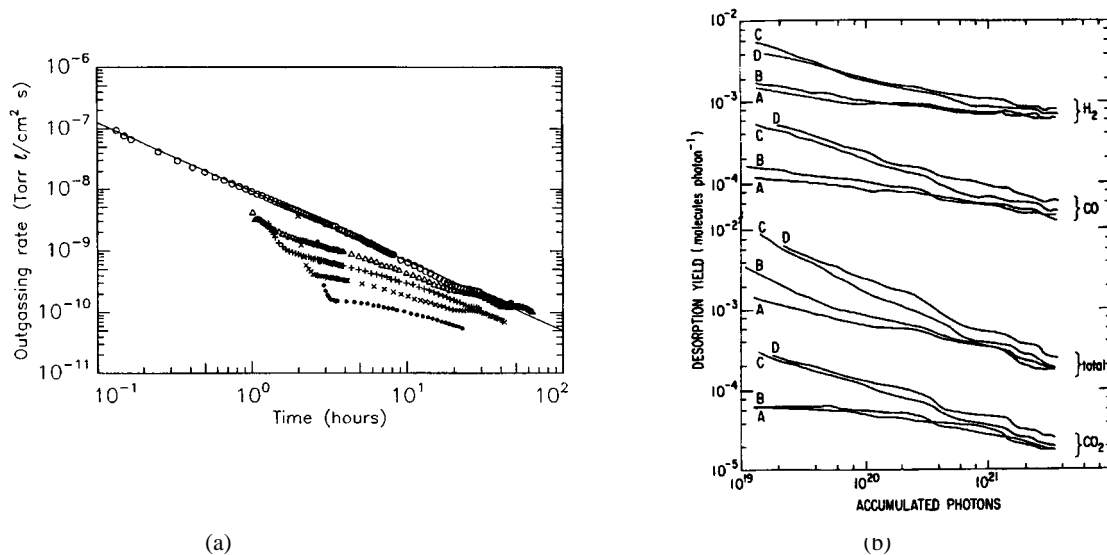
Fig 5: (a) The effect of glow discharge cleaning on total outgassing rates. Between each curve (from top to bottom) is a further "dose" of *in-situ* glow discharge (taken from Li and Dylla, J Vac Sci Technol **A13,** 1995, 572)

(b) The effects of various cleaning treatments on partial photo-desorption yields as a function of photon dose. We simply note here that the curves labelled "A" are after a glow discharge (taken from Hseuh and Cui, J Vac Sci Technol **A7,** 1989, 2418)

10.4 Air Baking

This procedure involves baking vacuum components at normal bake temperatures (250°C) in air. It reduces outgassing rates considerably, particularly for hydrogen. It was thought to work by inducing a barrier oxide layer, but may simply work by depleting the hydrogen from the bulk.

The technique is much favoured in the gravitational wave detector community but its value for accelerators is unproven.

10.5 Chemical "Baking"

An interesting idea originating in Japan is to use a chemical which has a particular affinity for water to react with the water adsorbed on a surface in such a way that the reaction products are gases which may be pumped away.

One such chemical is dichloropropane where the reaction is

$$(CH_3)_2CCl_2 + H_2O \rightarrow (CH_3)_2C{=}O + 2HCl$$
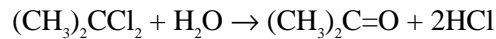
This technique is claimed (Tatenuma *et al*, J Vac Sci Technol **A16**, 1998, 263) to reduce the base pressure in a vacuum system by factors of 80.

However, the technique has to be carried out at a moderate temperature (80°C) so it is unclear what advantages this technique has in practice over a simple bake.

11. SAFETY

Safety is of paramount importance when choosing a cleaning process. For example, many processes use very hot liquids and/or large baths of chemicals.

Organic solvents, in particular, can be

- toxic (poisonous)
- flammable
- environmentally dangerous (e.g.ozone depleters)

When such solvents are used, it must be in properly designed plant suitable for the task. Vapour extraction and recovery systems must be installed. If the vapour is toxic or otherwise injurious to health, personnel should wear proper protective clothing and equipment, as well as individual monitors measuring their exposure to the vapour in the atmosphere. Alarms linked to atmospheric sampling monitors must be fitted near the cleaning plant. Breathing apparatus will be required when changing solvents and cleaning tanks.

If the solvent is flammable, then proper fire precautions will be required, including intrinsically safe electrical supplies.

When acids and alkalis are being used, neutralising pits and emergency neutralisation facilities and spill containment measures will be required.

Special buildings with controlled access may be required and rigorous operator training is essential.

12. COST

Cleaning to high standards can be costly. For large vessels and pieces of equipment, large cleaning baths are required, often containing many thousands of litres of expensive cleaning fluids which need to be changed regularly. Lifting and handling equipment which does not introduce contamination into the cleaning fluids, e.g. through oil drips, will be required.

The safety precautions outlined in Section 11 are expensive. It is therefore very important to clean only to the standard required and not to over specify a cleaning process as this will be uneconomic and wasteful.

13. HOW DO WE KNOW A SURFACE IS CLEAN?

There are two different approaches to determining whether or not a surface is clean. The more fundamental one is to perform a chemical analysis of some sort on the surface to determine what is there. Techniques are readily available to do this and the more common of these are discussed below. However, this does beg the question of what we actually mean by a clean surface. In much of surface physics and chemistry the answer is relatively straightforward since, in general terms, the experimenter will know what the "native" material is, be it a single crystal metal, an amorphous semiconductor film, or whatever. Anything else is "contamination" so the surface is "not clean".

However, when dealing with the real technological surfaces of vacuum vessels or components where the macrostructure of the surface is complex (as noted above in Section 10.2) it is by no means obvious what actually should be there. For example, in a low carbon steel, should surface carbon be regarded as part of the alloy or is it a contaminant? If there is excess chromium at the surface of a stainless steel over the bulk alloy concentration, is it a contaminant or is it an essential part of surface passivation?

Hence such analyses may raise more questions than they solve. In any case, they may or may not affect the controlled atmosphere we are seeking to obtain by using vacuum in the first place.

The second approach is more pragmatic and simply seeks to measure the properties of interest: if we want low pressures, measure outgassing rates; if we want low partial pressures of particular species in the residual atmosphere, measure them; if we want low desorption yields, measure them. To study the effects of cleaning treatments, one should measure in a systematic way how the properties of interest change. Unfortunately, few such systematic studies have been undertaken and published, so there are poor statistics on the efficacy of cleaning processes. This is why results in the literature are not definitive and why there are so many tenaciously defended but different recipes in the folklore.

14. SURFACE ANALYTICAL TECHNIQUES

14.1 Auger Electron Spectroscopy (AES)

AES is a surface sensitive technique which detects all elements except hydrogen and helium on a surface. The fundamental mechanism is illustrated in Fig 6. An incoming electron or photon ejects an electron from a core level of an atom to create a hole. This hole is filled by an electron falling from a higher energy level. The energy thus released is transferred to a third electron (the Auger electron) which is ejected into the vacuum.
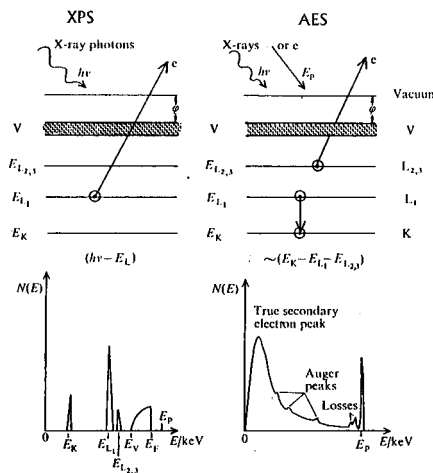

Fig 6: Principles of two types of electron spectroscopy – XPS and AES. (Taken from M Prutton, *Surface Physics*, Clarendon Press, Oxford, 1975)

The energies of Auger electrons are essentially fixed and depend only on the ejecting atom. Thus measuring a spectrum of such ejected electrons from a solid, when bombarded by electrons or photons, can perform a chemical analysis of the solid. Since the Auger electrons are at relatively low energy (less than a few hundred eV) they can only escape from the surface layers of the solid without being scattered and losing energy, so the technique is surface composition sensitive.

In practice the energies of the Auger electrons and the detailed shapes of the spectral lines vary slightly dependent on the chemical state of the emitting atom. Thus for example, it is perfectly straightforward to differentiate between a layer of graphite-like carbon, amorphous carbon or diamond-like carbon on a surface.
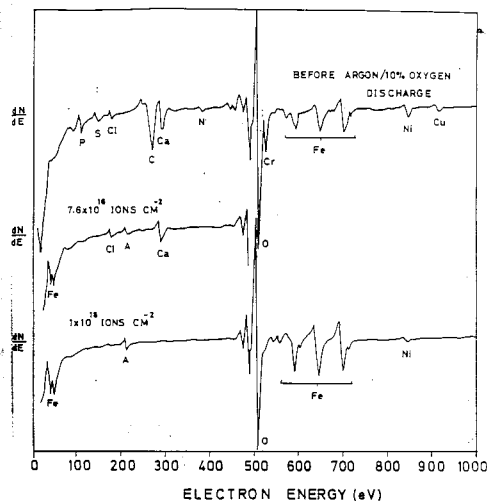
Fig 7: Auger electron spectra from stainless steel before and after glow discharge. Note how impurities such as carbon, sulphur and chlorine disappear, whereas the native iron peaks increase. Note also the implanted argon after the discharge.
(Taken from A Mathewson, CERN-LEP-VA/87-63)

The technique is quantitative and has a surface compositional sensitivity of about 0.1%, dependent on the species concerned. Typical spectra, showing the effect of glow discharge on a stainless steel surface, are shown in Fig 7. Note that these spectra are differentiated so that the spectral lines show up more easily against the background.

AES is essentially a small area sampling technique which cannot easily be used *in-situ* so tests are normally carried out on small coupon samples.

14.2 X Ray Photoelectron Spectroscopy (XPS)

This technique is similar to AES, but uses X-rays which penetrate somewhat deeper into the surface, although the emitted electrons may come only from the surface layers, dependent on their energy. The mechanism is again shown in Fig 6. Note that here what is detected is the first ejected electron i.e. the one which leaves the core hole behind. Subsequent relaxation can then be via the Auger process, so both types of spectroscopy can be carried out simultaneously. The energies of the photoelectrons are at a fixed value below the energy of the incoming photon, the difference being characteristic of the emitting species. The technique is quantitative, in principle being more sensitive than AES, although less surface specific. It is therefore difficult to quote a sensitivity figure for surface analysis. It provides much richer information on the chemical state of the emitter than AES. Again, it is a sampling technique.

14.3 Secondary Ion Mass Spectroscopy (SIMS)

This technique uses a beam of ions (often argon) to knock atoms off a surface. These are then detected as ions in a mass spectrometer. Both positive and negative ions are produced and, in principle, sputtered neutrals can also be detected. It is very sensitive but produces an abundance of information which is very difficult to interpret. It is semi-quantitative. The technique is useful for detecting compositional differences between different parts of a surface e.g. across a contamination patch. It is surface sensitive, provided a low energy and low intensity incident beam is used. Prolonged exposures can drill down through the surface layers and provide information on changes in composition with depth.

14.4 Laser Ionisation Mass Spectroscopy (LIMA)

This technique is similar to SIMS but uses a high intensity laser beam as the primary source of excitation. Ablation rates are generally higher than for SIMS so the surface sensitivity is lower.

15. PHENOMENOLOGICAL METHODS

As has been noted above, these essentially rely on measuring what one needs to know in order to achieve the desired result.

For vacuum purposes, these will essentially be measurements of total and partial outgassing rates or stimulated desorption yields, using photons, electrons or ions as appropriate. All of these techniques are discussed in detail elsewhere in these proceedings.

Although from a practical point of view it is difficult to apply these techniques quantitatively, by using standard methods, preferably in a single experimental station, it is possible to produce accurate *comparisons* of the efficacy of various cleaning techniques. Hence trends can be well established. It should be noted that it is very difficult to make meaningful quantitative comparisons between work carried out using different techniques and even between work in different laboratories using the same technique.

16. RECONTAMINATION

Once something has been cleaned, it may or may not remain clean! Care has to be exercised to ensure that it does not become recontaminated. The precautions required will, of course, be dependent on the degree of cleanliness required.

Some points to note are

- A vacuum surface should never be touched with bare skin. Clean, lint free gloves should always be worn and arms, etc., covered up

- The operator should take care does not to drop bits of himself/herself into the system, e.g. by wearing a hat or hood covering up hair and possibly the mouth and nose.

- All tools should be clean. Not just the business end, but also the handles, so that they do not transfer grease onto clean gloves.

- Smoking and the use of internal combustion engines should be prohibited near an open vacuum system.

- The gas used to let up the vacuum system should be clean.

- It should also be dry. Fig 8 illustrates the change in outgassing rate achieved by using nitrogen containing various concentrations of water vapour to let up a vacuum system.

- Nothing should be left in the system that should not be there, e.g. tools or rags.

- Vacuum items should be stored and transported under vacuum or dry nitrogen rather than being left open to the elements after cleaning
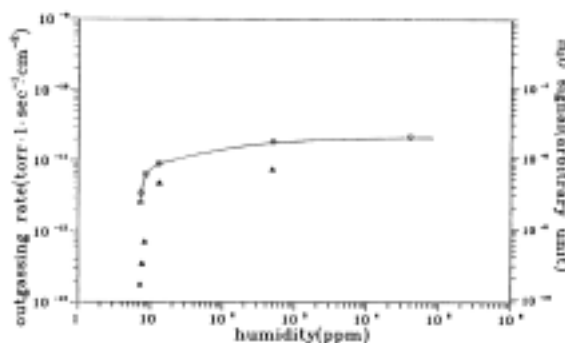

Fig 8: The outgassing rate and water partial pressure in a vacuum system after letting up with nitrogen containing varying concentrations of water vapour. (Taken from Liu *et al*, Vacuum **44**, 1995, 435).

17. SUMMARY

This paper has summarised briefly various techniques for cleaning vacuum systems and components and indicated what factors are of importance in choosing which should be used in particular circumstances. It has also discussed how one might be confident that a vacuum system is indeed clean enough for the purposes to which it might be put.

Nevertheless it must be strongly emphasised that it is only the users of any vacuum system who can determine what is required and if it has been achieved, so it is imperative that in any given situation suitable tests are carried out to establish that confidence.

SELECTIVE BIBLIOGRAPHY

The following list of references is extremely selective, but will provide the interested reader with sufficient further references to pursue.

Cleaning

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Procedures and specifications used at Daresbury Laboratory will be found on the World Wide Web at

<http://accelerator.dl.ac.uk/vacuum/docs.html>

These may be freely quoted and used, provided that due acknowledgement is made of their origin.