

3. Safety regulations

This operating manual provides advice for the safe operation of the ASU. With the help of this document the manager in charge of the installation must issue operating instructions that are binding for the operators. These operating instructions should contain among other items:



- Lists detailing the inspection intervals of safety valves
- instructions concerning abnormal operating conditions and malfunctions

The locally applicable safety regulations and rules for the prevention of accidents must be complied with during the operation of air separation plants!

This is also applicable to the storage, transport and further processing of the products obtained from the air separation plant.

Rules for the prevention of accidents and guidelines for the operation of air separation plants and the dealing with nitrogen in particular are published by the trade associations or other institutions.

The personnel employed in the plant must be instructed in respect of the following before starting work in the plant for the first time and subsequently at regular intervals.

- the operating instructions including repair and maintenance instructions
- the special risks involved in dealing with the gases and liquids of the plant
- the safety regulations
- the available safety equipment
- the measures to be taken in the event of accidents and malfunctions.

Any subjects covered and the time of such instructions must be recorded in writing and confirmed by the signatures of the persons instructed!

Further information regarding safety and operator training can be found in the relevant publications EIGA such as (also see attachments):

- IGC Doc 33/97/E "Cleaning of Equipment for Oxygen Service"
- IGC Doc 23/00/E "Safety Training of Employees"
- IGC Doc 04/00/E "Fire Hazards of Oxygen and Oxygen Enriched Atmospheres"
- IGC Doc 11/82 "Code of Practice for the Design and Operation of Centrifugal Liquid Oxygen Pumps"
- IGC Doc 44/00/E "Hazards of Inert Gases"
- IGC Doc 40/02/E "Work Permit Systems"
- IGC Doc 65/99/E "Safe Operation of Reboilers/Condensers in Air Separation Units"

Operating and safety instructions must be kept handy at any time for the personnel at suitable places in the working area.

The following notes and recommendations must be complied with to exclude and/or minimise possible danger from the operation of air separation plants and the dealing with the generated products.

However, these notes and recommendations do not claim to be complete.

Compliance with additional safety regulations applicable at the place of installation is imperative.

3.1. General characteristics of the air and its constituents

Constituents of the air: approx. 20.95 % oxygen
approx. 78.12 % nitrogen
approx. 0.93 % argon
remainder: noble gases and impurities (e.g. H₂O, CO₂, hydrocarbons)

Boiling point: -194.2°C (at 1.013 bar)

The air can be separated into its constituents by rectification.



As a result of the cold, direct action of liquid air on human skin leads to a destruction of tissue which is very similar to that caused by burns. If liquid air is left standing in an open vessel for a longer period, the oxygen content in the liquid will rise as a result of the evaporation of the more highly volatile nitrogen. This means that the liquid assumes more and more the characteristics of liquid oxygen.

3.1.1. Air Contaminants

Oxygen can react with a wide variety of materials. Therefore it must be manufactured, stored, and used in equipment that is kept free of contamination. Where contaminants cannot be completely eliminated sound design and safe operation practices enable them to be controlled within acceptable limits. For further information regarding this subject the operator is advised to turn to the relevant EIGA/CGA documents.

Contaminants may be introduced into an air separation plant by way of the air feed stream, by plant equipment malfunction, or inadvertently during maintenance or construction.

Airborne Contaminants

Particulate matter is normally removed from the air feed stream by filters on the suction side of the main air compressor. The contaminants of greatest concern are those which are flammable such as atmospheric hydrocarbons, some of which can pass through to the oxygen rich sections of the process system. Acetylene is of particular concern because of its relatively low solubility and high reactivity in liquid oxygen. Nitrous oxide is of further concern with respect to plant safety.

Control of Contaminants

The bulk of the contaminants are removed safely along with carbon dioxide CO₂ and water vapour H₂O in the molecular sieve adsorber. Only light hydrocarbons such as methane CH₄ and ethane C₂H₆ pass through into the cold box (if concentrations are high enough in the air ethylene will also enter). Nitrous oxide N₂O is only partially removed. The withdrawal of sufficient quantities of liquid oxygen from the sump of the low pressure column, the crude and the pure argon condenser vessels will ensure that the residual hydrocarbon and N₂O levels remain at a safe level for continuous operation.

Molecular Sieve

The specified operation cycle times, air and regeneration gas pressures, temperatures and flows, - with a special attention to air inlet temperatures - should be maintained within the limits specified in chapter two of this manual. If the plant is stopped the cold box inlet valves must be shut tightly to prevent desorbed contaminants passing forward into the plant. Downstream of the molecular sieve unit the CO₂ analyser is installed to monitor the performance of the unit. The operator must start switching to the regenerated bed immediately if a CO₂ content of more than 1ppm is detected. If the other bed is not sufficiently regenerated the ASU must be shut down to avoid ingress of hydrocarbons into the cold box.



Special attention must be paid to avoid depressurisation of the molecular sieve in the upward direction after or during a shut down of the plant. If the molecular sieves have to be depressurised always ensure that the gas is vented off upstream of the molecular sieve vessels. Never allow a valve to be opened downstream of the vessels to depressurise a bed. When the pressure in the vessel is falling and gas flowing upwards water vapour from the activated alumina in the lower section of the vessel would be desorbed and moved upwards where it would contaminate the molecular sieve in the upper section of the vessel. If water vapour manages to break through into the molecular sieve section of the vessel it will seriously and permanently diminish its capacity to adsorb hydrocarbons.

Reboilers and Condensers

The main condenser in the low pressure column condenses air or nitrogen against liquid oxygen. A decrease in the reboiler liquid level below the level where the thermosiphon effect occurs has the potential to concentrate hydrocarbon contaminants to a hazardous level. In this case dry evaporation might occur locally resulting in solid hydrocarbons depositing on the surface of the exchanger. For this reason the condenser must be operated at the specified level to maintain the boiling surfaces fully wetted. To achieve this, the condenser in the LP column must be operated 100% submerged.

The same principle applies to the crude argon column condenser and the pure argon condenser: Here too submergence of 100 % is required.

The requirement to run the condensers/reboilers at the specified submergence must not be mixed up with the distance between the level taps. The control system indicates the submergence i.e. the relative level compared to the geometric length of the condenser. Therefore the indicated level can exceed the 0-100% range.

Acetylene, because of its low solubility in liquid oxygen presents a particular problem. When its concentration exceeds the solubility limit, solid acetylene can collect on the surface of the liquid or on the walls of the reboiler passages, where it creates high local concentrations capable of detonating. The presence of acetylene in liquid oxygen, when detected, requires immediate investigation and corrective action. It should be checked, whether a higher concentration of hydrocarbons can come into the intake of the air compressor. In principle the purge flow has to be increased if the air is polluted heavily, it can even be necessary to shut down the whole air separation plant. This is e.g. the case, if CO₂ breaks through.

Purging

To prevent undesirable concentrations of hydrocarbons building up in vessels or drain lines continuous liquid purging and/or drain valve blow down must be carried out as specified in the plant operating instructions. The crude argon condenser must be purged permanently. The automatic purge valve has to be open at all times in order to purge the liquids out and keep impurity concentrations below the required level. The vessel is analysed for hydrocarbons which directly indicates insufficient purging.

In order to avoid any hazards, the following recommendations have to be strictly adhered to:

- The plant has to be warmed up every 3 years. All solid depositions of hydrocarbons, H_2O , CO_2 or N_2O , which may stick in the pipes, dead piping ends or heat exchanger fins are melted and vaporised. If the liquid levels in the reboilers are not kept at or above the required value, the re-circulation rate in the reboiler is decreased and dry vaporisation might occur which may lead to the local formation of deposits. These deposits may stick to the fins on the bath side of the reboilers and ultimately clog up passages leading to sufficiently high accumulations that would promote an explosion of the entire block. Especially N_2O which is not totally adsorbed in the molecular sieve unit can plug the fins of reboilers. Therefore the following guidelines applying to all condensers/reboilers have to be followed:
- If during normal operation or a plant load change the level should drop below 30% of the normal operating level for 60 minutes or longer all remaining liquid has to be drained.
- If during a cold standby period of one or two days the liquid level has been reduced to 80% or below of its normal level, either liquid must be added using liquid nitrogen injection, or all liquid in the plant must be drained.
- For cold starts after a short shutdown generally up to a period of 8 hours after a shutdown, the plant will have sufficient liquid to maintain the levels in the reboilers during its restart. Keep the liquid level under control and at a level of at least 80 % of its normal submergence value. Return the submergence level to the normal operating level as soon as possible. Liquid injection, if available, is recommended at this stage. A temporary drop of submergence level to 50 % is allowable for a short period. If liquid injection is not available other process steps should be considered (e.g.; reduce the incoming air to the process).
- For cold start after a long shutdown if the liquid in the reboilers falls below 80% of the normal operating level, it is necessary to drain the liquids from the reboilers prior to restarting. All the dead ends where liquid could be trapped shall be periodically purged.
- During start-up from a condition which begins with significantly lower than normal submergence level, it is important to first rebuild this level prior to bringing the oxygen to purity.

If one of the above stated criteria is violated the manufacturer has to be contacted or the part of the plant in question must be defrosted.

Monitoring of contaminants

Most hydrocarbons entering the plant are removed by the molecular sieve except for methane and ethane which are not readily adsorbed. The molecular sieve adsorbs contaminants in a particular order. Therefore a CO₂ analyser is installed to monitor the CO₂ content entering the cold separation process. Water, propylene and acetylene are adsorbed before CO₂ breaks through the molecular sieve. Those hydrocarbons which can enter the oxygen reboiler are readily soluble in liquid oxygen. Samples of the air feed stream on the downstream side of the molecular sieves may be checked periodically for signs of increasing hydrocarbon contamination, especially when atmospheric pollution levels are known to be high. The crude argon condenser and the LP column sump should be checked regularly using the C_nH_m analyser showing the hydrocarbon content. In accordance with the EIGA IGC Doc 65/99/E the hydrocarbon content must be below the following values:

Component		Maximum Allowable Concentration (vppm)
Methane	CH ₄	500
Acetylene	C ₂ H ₂	0.5
Ethylene	C ₂ H ₄	200
Ethane	C ₂ H ₆	250
Propylene	C ₃ H ₆	35
Propane	C ₃ H ₈	100
C4 Hydrocarbons		5
Total hydrocarbons (THC as CH ₄)		500
Carbon Dioxide	CO ₂	4
Nitrous Oxide	N ₂ O	100

Contaminants introduced during maintenance

Maintenance work that requires an opening up of the process system may accidentally permit entry of contaminants or unsuitable materials. Particular care must be taken during maintenance so that only proper materials and parts are used and that all new systems, parts and components are appropriately cleaned.

3.2. Protective measures

The following protective measures must be complied with strictly in the area of air separation plants and equipment for storage, transport and further processing of the generated products:

3.2.1. Fire and explosion hazard

1. No smoking and open fire. Work involving the use of fire, such as welding, soldering, grinding, etc., is forbidden as a general rule.

Special attention must be paid to avoiding unintentional ignition sources.

In the case of necessary servicing, repair or modification work it must be ensured that there is no inadmissible oxygen concentration in the ambient air inside and outside apparatus parts and that such concentration cannot occur during the work. Work of this kind must only be carried out under safety measures laid down in work permits and under the supervision of a responsible person.

2. Special attention must be paid to avoiding unintentional ignition sources.

To avoid unintentional sparking the use of shoes equipped with metal nails or fittings is not permitted.

Electrostatic charging of clothes and shoes has to be prevented by a suitable choice of materials.

3. All plant parts coming into contact with oxygen must be cleaned for oxygen operation and be clean as far as technically possible to guard against ignition hazard.

They must be free from:

- Loose parts or parts which can be loosened by the operation, such as slag, rust, welding residues, blasting material, oil, grease and solvents as well as other foreign matter and particles like packing material, anti corrosives and machining chips.

Contact with oily cleaning cloths or greasy fingers must be avoided. Cosmetics containing grease may become a source of danger. Clothing contaminated with oil or grease must not be worn.

For notes on cleaning methods and cleaning agents refer to chapter 3.4.

4. Storage of combustible materials in the area of the plant is forbidden, with the exception of the consumables and lubricants required for operating the plant.
5. Oxygen enrichments in the air must be avoided. Where such enrichments occur nevertheless or where they can emerge, such areas must be marked and instructions must be given for increased precautions to be taken. Adequate ventilation of such rooms must be ensured.

Prior to the inspection of oxygen bearing vessels and pipe lines, such vessels and pipe lines must be adequately purged with oil free dry air. Check analyses must be made to prove that an increased oxygen concentration does not exist. Instead of air, oil free dry nitrogen may also be used for purging, if it is ensured that the nitrogen concentration is eliminated prior to the inspection of the purged spaces (see chapter 3.2.2 regarding danger of suffocation).

6. Avoid staying in areas with increased oxygen concentration. Persons who have stayed in an oxygen enriched atmosphere nevertheless must suppose with certainty that their clothes are saturated with oxygen. Their clothing must immediately be aired thoroughly.
7. Oxygen shut off devices must be opened and closed slowly but continuously. Avoid jerky operation of shut off devices.
8. In plants equipped with a molecular sieve adsorber for cleaning the process air, acetylene and some other hydrocarbons are completely removed before the air enters the cryogenic section. For this reason, measurements of the acetylene content in liquid oxygen can be dispensed with. In order to extract all other hydrocarbons previously not removed completely, at least 0.15 % of process air feed to the rectification system must be withdrawn as liquid oxygen or oxygen enriched liquid from the LOX boiler. If the hydrocarbon content of

the ambient air is higher than normal the purging quantity must be increased. This quantity is sufficient, if loading and regeneration of the molecular sieves are carried out according to the operating instructions and progress without any problems. Possibilities of checking consist in monitoring the operating and regeneration temperatures and with the installed CO₂ analyser, in the monitoring of the CO₂ content in the cleaned process air. The CO₂ content at the end of an adsorption cycle should not exceed 1 ppm.

In the event of an unusually high hydrocarbon concentration in the feed air, e.g. natural gas release, special measures must be taken - increasing the liquid volume to be discharged, if possible, measurement of the hydrocarbon content. In the case of extreme conditions, the plant must be shut down.

9. Lubricants

If lubricants are used for machines (compressors, pumps, etc.) the special instructions by the machine manufacturers must be adhered to.

Lubricants may be used for valves and other apparatus parts only, if they have been tested by a recognised test institute with the result that they are suitable for use under the operating conditions from the safety point of view. Lubricants should preferably be dispensed with.

3.2.2. Danger of suffocation

Enrichment of the air with nitrogen or gases having a similar effect must be avoided. Where such enrichments occur nevertheless or where they can emerge, such areas must be marked and instructions must be given for increased precautions to be taken. Such rooms must not be entered without a respirator.

Personnel must not be allowed to stay or work within areas with increased nitrogen concentration or in areas where such enrichment may occur.

If work has to be carried out in such areas, make sure that an increased nitrogen concentration does not exist and cannot occur either.

Before rooms or vessels at risk from nitrogen are entered, check analyses must be made to prove that danger from increased nitrogen concentration does not exist.

The work must only be carried out under safety measures laid down in work permits and under the supervision of a responsible person.



Nitrogen can be used as instrument gas. Attention has to be paid to areas where the use of instrument gas can lead to increased nitrogen concentrations in this case.

The molecular sieve also adsorbs nitrogen. Therefore the vessels have to be treated like areas with increased nitrogen concentration.

3.2.3. Danger from cold

1. When handling cryogenic liquids, appropriate clothing (gloves, goggles, tightly woven clothes, trousers overlapping the boots) must be worn for protection against contact with the liquid.
2. As a result of liquid vaporisation, the air is enriched with the vaporised medium.
3. Before the cryogenic section is entered, a work permit has to be obtained. The area concerned must be heated to ambient temperature. Attention is drawn to potentially increased oxygen and nitrogen concentrations.



While disposing cryogenic liquids into the vaporiser persons might come into contact with low temperature gas or liquid. Safe operation has to be ensured and the venting must be observed at all times.

3.3. Protective equipment

3.3.1. Buildings and plant areas

- Escape routes in adequate numbers from rooms and plant areas as well as access ways for fire brigade vehicles must be marked and kept clear at all times.
- Rooms in which process gases may escape under normal operating conditions must be ventilated in such a manner that no inadmissible nitrogen or oxygen concentrations may arise in the room air. If natural ventilation is inadequate, forced ventilation by fans or similar equipment is required.
- Special attention must be paid to the ventilation of cellar rooms, pits and channels.
- In areas where liquid oxygen leakage is possible, the floor must only consist of non combustible material (e.g. no tarmac, wood, etc.). The floor should preferably be free from joints and pores.
- Discharge or ingress of low temperature liquids into the sewage system or cable pits must be prevented (e.g. by water seals).

3.3.2. Fire protective equipment

Special local and official regulations must be followed.

Preferably portable CO₂ fire extinguishers in adequate numbers must be installed for fire fighting in the control room, analysis rooms and switchgear rooms. These must be easily accessible. Portable powder hand fire extinguishers must preferably be provided in the vicinity of machines.

Smoke detectors and fire water hoses have to be installed.

3.3.3. Equipment protecting against overpressure

All vessels and pipe line systems which are pressurised or in which pressure may build up are equipped with overpressure protection (safety valves, bursting disks).

This overpressure protective equipment must be kept in serviceable condition at all times. The correct blow off pressure setting of safety valves must be checked and readjusted as required at regular intervals in a written manner.

3.3.4. Reliable functioning of protective equipment

All protective equipment must be kept in good operative condition at all times. Alarm and safety devices must be checked in regular intervals. A documentation of this work is required.

3.4. Cleaning methods and cleaning agents

Adequate cleaning can be performed according to various methods. The cleaning methods must be matched with the plant parts to be cleaned, e.g. the point of application, kind and size, and with the nature of the contamination.

3.4.1. Examples of cleaning methods

Immersing, flushing, washing, spraying or wiping with lint free cloths drenched with solvents.

To be applied for removing contamination by oil and grease.

When selecting the cleaning agents, statutory regulations (e.g. regarding the use of CFC) as well as the supplier's application and safety instructions must be noted and complied with.

Normal tri chloride ethylene ($\text{CHCl}=\text{CCl}_2$) must not be used for cleaning aluminium and aluminium containing light metals because an explosive reaction might take place.



Make sure that all contamination and residues of cleaning agents are completely removed from cleaned plant parts as far as this is technically possible.

Depending on the cleaning agent and the application, residues can be removed, for instance, by

- blowing through with oil free air or oil free inert gas
- flushing with water of reasonable quality, followed by drying, if aqueous cleaning agents have been used
- drying and vaporising

3.4.2. Blasting

To be applied for removing all foreign matter on surfaces of insensitive parts and on straight pipe sections.

Glass, steel or slag must be used as cleaning medium.

3.4.3. Pickling

To be applied for removing rust and scale on steel.

Pickling agents, concentration, application temperature and neutralisation must be agreed between the manufacturer and the user. Additional loading resulting from the weight of liquid pickling agents must be taken into account.

3.4.4. Blowing through

To be applied for removing foreign matter which are loose or can be loosened from the system.

3.5. Safety instructions for inspection, service, repair or modification work

The mentioned work must be carried out on a plant which is or has been in operation only under the safety and protective measures determined in writing in a "permit" issued by a responsible person in charge of such work.

In the main, the following must be noted:

- The rules for the prevention of accidents in force.
- Adherence to the protective measures as per chapter 3.
- Safe and tight disconnection (e.g. isolation of valves, removal of spool pieces or insertion of isolating disks) of process gas sources which could cause an inadmissible change of the normal oxygen to nitrogen ratio in the working area.
- Relieving the system from pressure.
- Purging of process gases.
- Possibly heating or cooling.
- Monitoring of the allowable oxygen and nitrogen concentrations in the working area before the beginning and during the work.
- Possibly performing the work with a respirator.
- Supervision of the work from a point outside the danger zone.
- In the case of work on plant parts difficult of access, necessary safety precautions against falling must be taken (e.g. using a rope and a safety harness).
- Check of the necessity and availability of fire extinguishing equipment as well as first aid measures.