Argon Re-condenser, WBS 5.2.5 **Flare Note LAR 60**

Heat conducted through the tank walls and other gas sources must be removed by the argon re-condenser.

A summary of the heat loads for the two tank sizes.

Tank size	50k ton	15k ton
tank heat load	47 kW	20 kW
flash during filling, with 34 kPa(gage) supply pressure	6 kW	6 kW
vapor displaced during filling	1.5 kW	1.5 kW
Total with 1.25 factor	68 kW	34 kW

Multiple argon condensers will be located in the gas space of the detector tank. Coiled tube heat exchangers would be compact and can be made with low thermal stress. The design would include five active heat exchangers and five installed spares, all located in the gas space of the detector tank. For the 50k ton tank each heat exchanger would have a surface area of 7 m^2 and would occupy a volume of 1 m^3. The heat exchangers in the 15k ton tank would have a surface area of 2 m^2 and a volume of 0.3 m^3. Liquid nitrogen will be circulated through the condensers. Spare condensers will be installed, so if a leak should develop, the offending condenser can be isolated from the nitrogen circuit. The condensers will be designed for low thermal stresses and leak tested. Condensers like this are available commercially.

Liquid nitrogen will be stored in a tank near the detector tank. A pump with an installed spare will deliver nitrogen to the condensers. The nitrogen will partially boil in the condensers and exit with the quality less than 0.4. The two-phase nitrogen will return to the storage tank which has the additional function of a phase separator. Reliable liquid nitrogen pumps are commercially available. The spare pump will automatically start if the lead pump fails to run properly.

Liquid nitrogen may be provided with a liquefier, a liquid delivery system or both. A liquefier can run automatically with little operator effort. Equipment down time can be covered with spare equipment or a liquid nitrogen supply. A generator would cover power outages, expected to be frequent at the remote site. Operators would be needed for maintenance and to respond quickly in case of malfunction. Cosmodyne offers a standard refrigerator that can easily handle the 15k ton tank. The larger tank would probably require a custom design. At least two other suppliers could supply a refrigerator as well.

Liquid nitrogen may be delivered by truck or rail. Truck deliveries can be completely handled by the supplier, but railcars would have to be connected by local operators. Deliveries are susceptible to weather or other scheduling interruptions. The amount in discussion here is less than the consumption at Fermilab, which uses a combination of a liquefier and truck delivery.

Liquid nitrogen consumption

Tank Size	50k ton	15k ton
Liquid nitrogen consumption	31 tons/day	15 tons/day
truck supply	12/week	6/week
rail car supply	5/week	2/week
Fermilab Liquid Delivery	41-71 tons/day	

Regardless of the condensing system there are times when it could malfunction. The tank ullage space will pressurize quickly should all cooling fail. Detector tank venting will be start within ten to thirty minutes after cooling failure. Argon loss would be 1 ton/hour for the larger tank and 0.5 tons/hour for the smaller tank. A vent valve system must be designed to prevent air from entering. This might consist of two valves in series with a purged space between them, and a pipe with enough length and velocity to prevent backflow along pipe walls.

A reliable control and interlock system will be needed to maintain tank pressure. If the tank relief valves operate for high tank pressure or especially for tank vacuum a serious disruption would occur. A SIS(Safety Instrumented System) would presumable be used to reduce the possibility of relief valve operation.

The tank will be equipped with safety valves, which may also require special purging procedures to minimize argon contamination while the valves are closed.

R&D for the re-condensing system

1. A cost comparison of refrigeration vs. liquid delivery would include installation, operating effort, utility connection, utility consumption, liquid supply, downtime analysis and other considerations.
2. Condenser performance testing should be done to confirm design calculations.
3. Review the literature on tank rollover and evaluate if it could occur in this case.
4. Natural convection has been analyzed for a full tank, but should be analyzed further to include wire planes and field cages.
5. Evaluate whether bubbles can form anywhere in the tank, especially around hot spots such as tank restraining bars.
6. Review barometric pressure data for extreme absolute values and maximum rates of change.
7. Design and test vent valve system.
8. Design and test relief valve sealing or purging system.

Argon Filling WBS 5.2.2

Liquid argon supply

Liquid argon may be delivered by truck or by rail car. The possibility of using a local air separation plant was discussed with Praxair, who felt it would be more feasible to use existing facilities and ship the liquid. Multiple suppliers could be used if necessary to reduce the filling time. The same filling rate is being considered for both 15k and 50k ton tanks, the rate being limited by argon supply and purification rate.

Argon purity is a variable that must be specified carefully. Most of the discussion has involved oxygen since it is both a common contaminant and has a high affinity for electrons. Other gasses such as HF6, while not common in air, could seriously reduce the electron lifetime. So the specification must be based on electron lifetime, with specific guidance regarding possible contaminants. Electron lifetime testing would be done both at the air separation plant and at the receiving station.

Oxygen concentration has been discussed with Praxair and our experience at Fermilab has been considered. A delivered oxygen concentration of one ppm is reasonably priced, requires careful but not difficult handling procedures and can be maintained without purification. For example the same argon has been in use at Dzero for twelve years without degradation or purification.

Argon Receiving

A proven procedure was used at Dzero, NWA and E706 for receiving liquid argon. This procedure would be used for Flare as well, on a larger scale. It would take 3000 truck loads to fill the 50k ton tank, 1000 truck loads to fill the 15k ton tank, so an efficient and effective means of receiving, purification and testing is needed. The procedure for rail cars or trucks would be the same, but rail cars are 2.5 times the size of trucks. The intermediate storage tanks would be cooled by circulating liquid nitrogen through argon condenser coils. The coils might be external or internal to the storage tanks. Just as with the detector tank provisions will be needed for venting in case of cooling failure and preventing diffusion back through closed relief valves.

Procedure:

1. Connect loading arm to truck
2. Evacuate receiving line and fill from supply truck, repeat if necessary.
3. Analyze the supply liquid with electron lifetime monitor, oxygen monitor and perhaps other instruments.
4. If the load is acceptable, drain or pump into intermediate storage tank.
5. Pump liquid from intermediate storage through purifier into high purity storage tank.
6. Analyze liquid before and after purifier and from second intermediate storage tank.
7. Pump into detector tank.

Failure scenarios that might be associated with receiving argon include adding contaminated liquid to the detector tank or spilling argon during the connection. The liquid will be repeatedly analyzed before it enters the detector tank. If the electron lifetime meters indicate a problem, a chromatograph or spectrometer might be used to determine the type of contaminant. At very low concentrations it may not be possible to determine an unknown contaminant. A spill during connection could cause personnel injury from frostbite or asphyxiation. The risk will be reduced by having good equipment on hand, having written procedures for normal and abnormal situations, training operators etc.

truck or rail car unloading arm

Proposed R&D

1. Make a list of known electronegative elements and compounds with their electron affinity.
2. Determine whether rail cars may be drained by gravity or pressure or if a pump is needed.
3. Determine what means of replacing the liquid volume inside the supply tanks should be used.
4. Select a pump, loading arm or hose, and other handling equipment that would be suitable.
5. Evaluate time needed to connect and test arriving trucks and cars. Determine how many unloading stations are needed.
6. Draw a Process Flow Sheet with heat and mass balances.
7. Draw a P&ID.
8. Write a specification for piping, valves and other wetted components that will handle the purified argon.
9. Discuss the possibility of an air separation plant with potential suppliers.
10. Evaluate the possibility of selling the argon at the conclusion of the experiment.

Purification, WBS 5.2.3

FLARE note LAR-56 discusses Argon purity and purification and makes a number of important points about sources of contamination and contamination over time. This description is meant to build on that paper, and to discuss the proposed R&D. While electron lifetime is the primary goal, the most common electro-negative gas is oxygen. This discussion revolves around oxygen, but other possible contaminants must be considered as well. The oxygen goal is 50 ppt(parts per trillion) oxygen in the detector tank liquid in a reasonable length of time.

Tank Cleanliness

Construction Materials and Methods
Steel tank construction commonly includes marker pens, dye penetrants, lubricants, and other possible contaminants. A list of prohibited materials should be developed that might contain halogens or other electro-negative components.

Vacuum box leak checking or ultrasonic leak checking will be done on all welded joints in the tank. Individual leaks down to 10^{-3} atm cc/sec can be detected this way. The leak testing should be done or verified by an independent inspector.

Lap and butt welded joints normally used in tank construction will preclude having large dead volumes in the shell and bottom. But the internal structures for roof support, wire support, etc. must be designed to avoid any dead volumes that could contaminate the argon for a long period of time.

Tank Cleaning
The tank will need to be cleaned after hydro-testing. Construction dirt, grease and oil stains, marker pens, lake water sediment, and bugs must be removed. Any heavy oil or grease stains will be removed with an alkali cleaner. Following that the entire tank would be cleaned by spraying or wiping a mild acid with a surfactant and possibly a solvent, followed by a clean water rinse. The choice of acids will depend on their reaction with the parent metal, cleaning effectiveness, and electro-negativity. The stainless steel tank for Icarus was pickled and passivated with nitric acid, rinsed with de-mineralized water as reported in Flare note 56. An inhibitor may be added to lower the amount of steel removed. The effectiveness of this cleaning would be affected by surface finish. Tank construction is normally with 'as-rolled' steel plates with a surface finish of 125 micro-inches or rougher. Mechanical finishing in the shop should be considered to ease cleaning.

The surface area of the detector and field wires is appreciable and must be cleaned as well as the tank walls. Possible metal removal precludes acid rinsing, but it might be necessary to run wires through a solvent bath prior to hanging. This might be done at the wire manufacturer and followed with secure packaging.

Air Removal

Gas purge and outgassing

Initially the air in the tank is removed by purging with argon gas. The argon gas is introduced at the bottom and vented at the roof. LNG tanks are normally purged this way with nitrogen gas to reduce oxygen concentration and can achieve 1% oxygen. The higher density difference between argon and air should produce better results. Nitrogen and moisture will be removed proportionally. To obtain the best results it might be necessary to use diffusers. Diffusion calculations would better show how far this purge could go. If the tank is purged to 1% oxygen, then in the 50k ton tank the major air contaminants remaining would be:

Oxygen	500 kilograms
Nitrogen	1600 kilograms
Water	70 kilograms

Diaz extrapolated the Icarus outgassing data and estimates the 50k ton tank warm outgassing to be:

Oxygen	120 grams
Nitrogen	310 grams
Water	2700 grams

Diaz suggests the tank be dried by heating to 120C. Any temperature increase would increase the water outgassing rate, but there could be problems with thermal expansion.

Rough purification

The amount of oxygen left after gas purging is ten times the amount that would be introduced if the tank were filled with liquid at 1 ppm. The high purity system is not well equipped to deal with large amounts of oxygen or other contaminants.

Rough purification of the warm tank has the advantage of the highest outgassing rates. Oxygen and other contaminants might adsorb to tank shell and other surfaces when cold, but they could present a persistent, slow source of contamination. If the tank is purified warm, this concern is reduced. Rough purification equipment might also be used to accept higher contamination in the supplied argon.

Five possible methods could be used to remove this oxygen left over from gas purging and from outgassing.

1. Fill the detector tank with a small amount of liquid and operate the main purifiers. This was discussed in Flare note 56.
2. React the oxygen with copper. This can produce purity below 1 ppm. It does not remove other contaminants. It could also be reacted with lead selenide and possibly other reactants. However David Artrip of BASF does not recommend using their copper reactant above 500 ppm oxygen.
3. Adsorb the oxygen with molecular sieve or activated carbon, probably at 90K. This can produce purity below 1 ppm and will also remove water.
4. Inject hydrogen and flow the mixture through a catalyst, then remove the water with phase separation and molecular sieves. This can reduce oxygen below 1 ppm and also removes water.

5. Remove the oxygen with a 200 tray column. This is a relatively new technology and might be able to produce 1 ppm oxygen concentration, but columns this size would be large and complex. Could discuss further with Cryogenic Consulting Service, Inc. http://www.cryogenic-consulting.com/

Discussion

1. <u>Purification with liquid argon.</u> The detector tank would need to be filled to a depth of 0.6 meters for the circulation pumps to operate. This will require the addition of 260 tons of argon, two thirds of which will remain in the vapor phase. If this liquid is circulated through a purifier and returned to the tank. Oxygen in the gas would be adsorbed by the liquid and subsequently removed by the purifier. Starting with an initial concentration of 1% in room temperature gas, the additional argon brings the oxygen concentration down to 2400 ppm. This liquid can then be run through a molecular sieve. It is not feasible to run this through the Air Liquide Ultral purifier. It would be saturated in less than two minutes at the normal flow rate, and then a ten hour regeneration would be required.

2. <u>Reaction with copper.</u> The copper catalyst BASF R-3-11 is a copper layer deposited on molecular sieve surfaces. It has can collect 60 grams of oxygen per kilogram of catalyst. (Experimental study on oxygen and water removal from gaseous streams for future gas systems in LHC detectors, CERN, 2000)

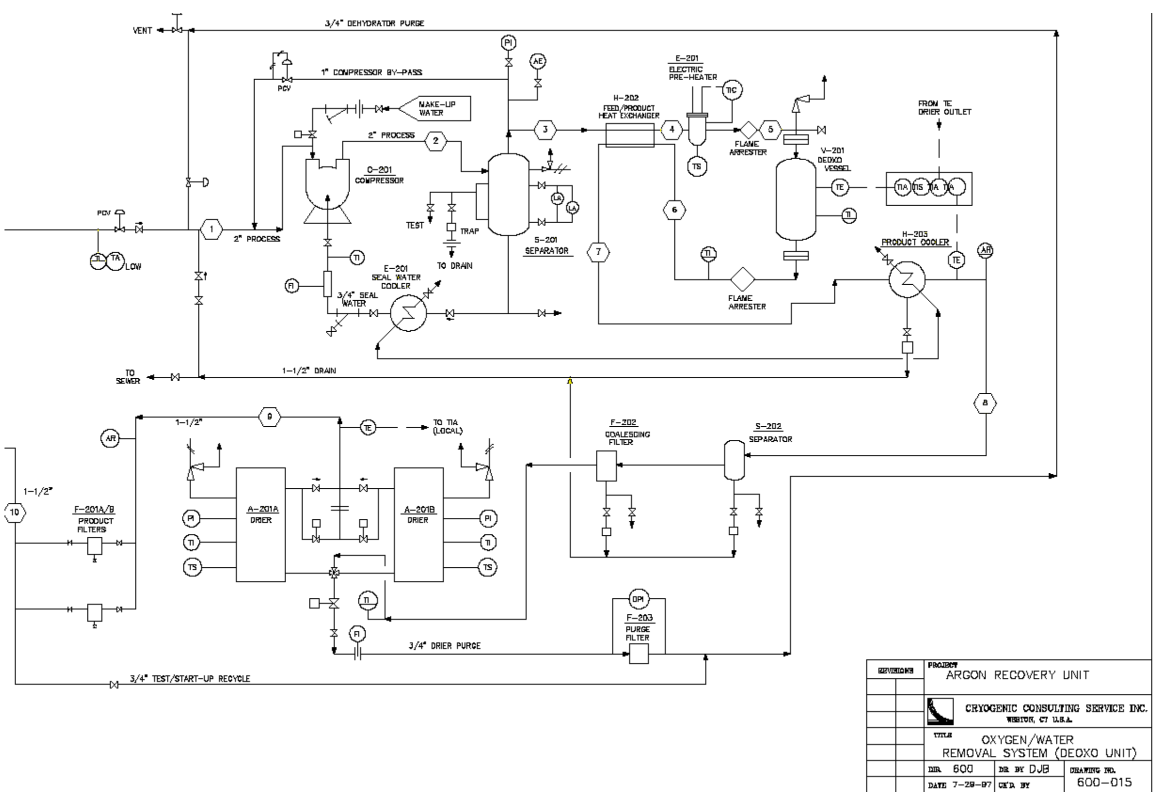
A 200 kg bed of BASF R-3-11 would remove 12 kilograms of oxygen before requiring regeneration. With a flow of 14 kg/min starting at 1% oxygen in the tank, the bed would be saturated in one hour. As contamination decreases the run time will increase. Assuming the tank is completely mixed, the tank reaches 1 ppm in three weeks, with fifty regenerations. Two or even three beds would be necessary to maintain the flow. The copper reactant would be preceded by a molecular sieve to remove water vapor. The compressor to circulate the gas might be a Sundyne centrifugal. This flow rate is mid-range for their compressor selections. The compressor motor size would be 33 kW.


Sundyne compressor with transmission

At least two other suppliers offer copper or 'active metal' oxygen removal products. Englehard Corporation produces copper alumina catalyst for oxygen removal. The amount collected is not readily available. Ridox Reagent offers an active metal on an aluminum substrate. A 200 kg bed would remove 140 kilograms of oxygen before requiring regeneration. Performance is dependant on flow rate and inlet oxygen concentration.

3. Physical adsorption of oxygen and nitrogen in argon is possible, probably at 90K. Papers have been requested with adsorption isotherms and other pertinent information. Adsorption is commonly used to achieve 1ppm impurity concentrations, but is very dependant on the composition, pressure and temperature. When these papers arrive the possibility will be evaluated further.

4. Reaction with Hydrogen. Most air separation plants achieve low oxygen concentration by reacting it with hydrogen. The argon is compressed; the same compressor discussed earlier would suffice. Hydrogen is injected slightly in excess of the stoichiometric concentration. The mixture is heated and passed through a catalyst where the reaction produces water. The gas is subsequently cooled, possibly condensing some of the water. The water is removed with phase separation followed by a molecular sieve. Water could be removed down to 1 ppm by the molecular sieve. The excess hydrogen remains in the stream. It could be removed along with nitrogen by distillation. In distillation, nitrogen separates from argon more easily than oxygen does. So the number of steps is estimated between 5 and 20, depending on the purity required. Or nitrogen might be removed with physical adsorption. When the adsorption data arrives it will be evaluated.



Tank Final Purification

Tank Liquid Circulation

During filling and for purity maintenance, liquid argon will be removed from the bottom of the detector tank, pumped through a purifier and returned to the top of the tank. The tank condition during initial purification was discussed by Adam Para "Argon Purity and Purification in a Large Cryogenic Tank". Following is a discussion about the equipment that could be used.

The flow rate will be 28 tons/hour. This is based on reasonable circulation rates and fits with two Air Liquide Ultral purifiers.

Pumps and detector tank outlet

The pumps may be internal to the detector tank or external. Internal pumps are sometimes used with LNG tanks to eliminate any connections below the top of the tank. Regulations require either substantial land area or internal pumps. There is no such standard for liquid argon tanks and an internal pump has several drawbacks, including

- External pumps would be much easier to repair, then evacuate and purge.
- Internal pumps must have a submerged motor which would be a contamination risk
- Internal pumps are more expensive since they require a large tube through the tank and a structure on the tank roof for lifting.
- Internal pump replacement would be a much bigger mechanical operation.
- The risk of draining the detector tank through drain pipe damage can be mitigated with internal valves, a careful mechanical design and maintenance of the tank bottom heaters, all of which are known technologies.

A circulation rate of 28 tons/hour cleans the tank in a reasonable time period and matches the capacity of two Air Liquide Ultral purifiers. This flow rate can be delivered by a 7.5 kW pump. An installed spare pump would be able to start on short notice if the lead pump failed. Centrifugal pumps are very reliable and need little maintenance. The pump may be equipped with seals or submerged motor, but most likely it will have a magnetic coupling, which eliminates seals and keeps the motor out of the argon.

Piping in this circuit must be built to high purity standards to avoid contamination. Most joints will be welded. When a joint must be dismountable, metallic seals will be used whenever possible. If a non-metallic seal is necessary, it will be double sealed and purged between the seals to limit air permeation.

High Purifiers

As an initial design we have assumed that the high purification starts at 1 ppm oxygen and improves the argon from there. 50k tons of liquid argon at 1ppm contains 50 grams of oxygen. Five commercial products are available to achieve the highest purity.

1. Messer Oxisorb

2. Air Liquide offers a packaged liquid purifier, $400k. Regeneration would consume $800k of argon during filling. Possibly can recover most of it.
3. Praxair offers gas purifier for $600k
4. (Trigon) offers regenerable adsorbent

Messer's Oxisorb can be supplied in custom containers. The Oxisorb is usually preceded by Hydrosorb in standard Oxisorb cartridges. The regeneration of the Oxisorb for Icarus was done at the Messer plant. Messer has not been forthcoming about the regeneration process, and if it meant shipping the cartridges back to Europe it would be a serious logistics problem. The Oxisorb produce data is based on gas service at room temperature, although Icarus reports good success with liquid argon. If 200 liter beds are used in liquid service, each bed would collect 2.1 kg of oxygen before requiring regeneration.

Air Liquide's Ultral purifier is built for the semiconductor industry which also has very high purity requirements. Nine of the packaged purifiers have been sold, so it is a proven product. The flow capacity is 14 tons/hour. It has the capacity to adsorb 700 grams of oxygen. Regeneration takes ten hours and consumes 5 tons of argon as well as some hydrogen and 280 kWH of electric power. The regeneration gas contains water which can easily be removed with an adsorbent, but it is not clear how the nitrogen leaves the purifier.

Trigon Technologies has two oxygen trap materials. The first type can remove oxygen to 2 ppb and the second, which has much less capacity, can reduce to below 1 ppb. They may be installed in series and can be regenerated on site with a heated hydrogen/argon sream. Trigon states the room temperature capacity data, but none is available for liquid argon. Based on the room temperature data, a 200 liter bed could collect 1.3 kg of oxygen between regenerations.

Proposed R&D

1. Evaluate cleaning methods for effectiveness with respect to surface finish.
2. Evaluate cleaning methods for electro-negative residue.
3. Evaluate disposal of cleaning fluid.
4. Write a specification for allowable dead volumes.
5. Study how hot the tank may be heated to increase drying speed.
6. Run an FEA analysis on gas diffusion during tank purging.
7. Size rough purification equipment more specifically for copper reaction, hydrogen reaction and adsorption both for purifying a tank of warm gas and argon delivered at 10 ppm.
8. How important are other air components such as nitrogen and carbon dioxide?
9. How much oxygen does Trigon collect in liquid argon service?
10. Test purification at PAB with evacuated dewars
11. Test purification at PAB with non-evacuated dewars
12. Evaluate four types of high purity systems
13. How is outgassing affected by argon atmosphere and low temperature?
14. How does the Ultral regenerate after absorbing nitrogen?

References

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Cennini, "Argon purification in the liquid phase", Nuclear Instruments & methods in Physics Research, 1993