Purification of argon from a diluted stream

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We report on the design, performance and commissioning of a cryogenic distillation column for low radioactivity underground argon purification that has been constructed at Fermi National Accelerator Laboratory. The plant accepts a mixture of argon, helium, and nitrogen with low argon concentration and is designed to return pure argon with a nitrogen contamination less than 10 ppm. During the commissioning, the distillation column in a continuous mode produced argon 99.9% pure. After running in batch mode, the argon purity was increased to 99.95%, with 500 ppm of nitrogen remaining. The argon production rate was about 1 kg/day.

INTRODUCTION

Argon is an attractive medium for direct searches for WIMP dark matter. Atmospheric argon, however, contains 1 part in 10^{15} of the radioactive isotope ^{39}Ar, formed by the interaction of cosmic rays on ^{40}Ar. The decay of this ^{39}Ar can limit the sensitivity of these dark matter searches, particularly at the ton-scale.

We have identified an underground source of CO_2 in Cortez, CO, containing traces (~ 500 ppm) of argon almost free of ^{39}Ar. This gas needs to be purified to remove all non-argon contaminants. The first purification step is performed locally by means of a Vacuum Pressure Swing Adsorption System (VPSA), and produces a crude argon stream, containing 3-5% of argon with a balance of helium and nitrogen [1]. The underground argon from this plant has an ^{39}Ar concentration less than 0.65% of the ^{39}Ar in atmospheric argon [2].

The argon-nitrogen-helium mixture is then shipped to Fermilab where we have built a cryogenic distillation column to remove helium and nitrogen and produce argon with residual contaminations at or below 10 ppm. The key element is the vertical separation column filled with packing material and along which a controlled temperature gradient is established. This presentation will detail the requirements, design, construction, and performance of the cryogenic distillation column that has been constructed for the purification of the gas extracted from the CO_2 wells in Cortez, CO.

The first use of this underground argon is in the DarkSide-50 experiment, scheduled to start operation in December 2012, which will use 150 kg. Eventually, it is expected that the column will process many tons of low-radioactivity argon, allowing the development of ton-sized detectors, among which are DarkSide Generation II and DEAP 3600, which will contain about 5,000 kg and 3,600 kg of Argon respectively. The column could also be used to purify other targets used in these experiments (Xenon in particular).

CRYOGENIC FRACTIONAL DISTILLATION

A cryogenic distillation column performs a separation between the components of a mixture by exploiting the different boiling points and relative volatility of the components. The more volatile component will rise to the top of the column, while the less volatile one will be collected as liquid at the bottom. The goal for this plant is to concentrate argon in the liquid phase at the bottom, and waste nitrogen and helium in the gas phase at the top. More specifically, we will produce argon with very low nitrogen concentration from the bottom.

We based the basic design of the distillation system on the McCabe-Thiele (M-T) method, one of the standard methods for the design and analysis of a distillation system [3, 4].

The main element in the distillation system is the column in which the gas-liquid equilibrium is maintained. The reboiler, at the bottom of the column, collects the liquid flowing down and boils part of the liquid using a heater. The condenser, at the top of the column, plays a critical role in order to maintain

a constant temperature profile along the column. The input gas is cooled down to a temperature just above the argon boiling point, and then supplied to the feed point in the column. The argon processed through the column, with a lower nitrogen and helium concentration than in the feed, is obtained from the reboiler. The waste stream, argon with a higher nitrogen and helium concentration, is collected from the top.

In the M-T method the distillation tower is assumed to be a connected series of theoretical stages, with the gas-liquid equilibrium changing by one step in each stage. The number of theoretical stages and the optimal position of the feed point are calculated for given boundary conditions of feed, waste and product flow rates, more volatile component concentration in the feed, waste and product, and reflux ratio.

Process simulations have also been performed in collaboration with Linde using UniSim simulation software, an engineering suite widely used by oil and gas separation processes companies. Several feed compositions have been analyzed with the argon concentration ranging from 10% to 90% with a nitrogen balance. 5% argon with a balance of helium (55%) and nitrogen (40%) has also been simulated. The results of the simulations are consistent with what already found with the M-T method and they also show the capability of the plant to run with a low argon content feed and to be able to produce argon at the desired purity and with a high recovery, above 95%.

THE EXPERIMENTAL APPARATUS

Figure 1 (left) shows the schematic of the cryogenic distillation column. The packing inside the column is a key element of the distillation system. We used the EX Laboratory Packing from Sulzer Chemtech (see Figure 1, right) with a diameter of 0.022 m. The liquid load of this packing is between 0.48 $m^3/(m^2h)$ and 4.84 $m^3/(m^2h)$. The HETP (Height Equivalent to Theoretical Plate) for this packing is typically 0.053 m for liquids (the specific value for argon was not immediately available from the company). The HETP depends strongly on the liquid load and on the type of liquid, so we conservatively increased this value by a factor two, therefore the total overall packing length is about 3.18 m, equivalent to 60 stages. We assembled the column with this configuration; in practice we could only fit 58 stages. The optimal position of the feed was estimated to be the 5th stage from the top, 0.53 m from the top with the M-T method, and the middle of the packing with the simulations. We thought that the simulations were more accurate and we selected the middle of the packing as feed position.

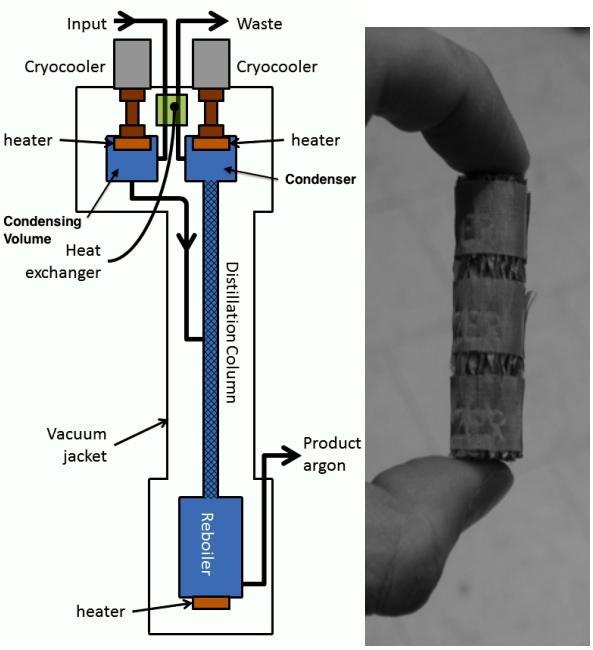

Figure 1 Cryogenic Distillation Column Schematic (left) and one element of packing (right)

The gas mixture is pre-cooled down through an heat exchanger, model GBM220H-60(3p) from GEA-PHE using the cold nitrogen and helium gases vented through the condenser. The cold gas mixture then enters the condensing volume where argon and nitrogen condense and eventually feeds the column. The condensing volume is a custom made cylinder, 0.18 m in diameter and 0.11 m high for a volume of 2.75E-3 m^3.

The cooling power needed to cool down and condense the feed is provided through a temperature-controlled cryocooler, model AL-600 from Cryomech, mounted on the top flange of the condensing volume. This cryocooler provides 600W of cooling power at 77K and it is coupled with a 600W heater and temperature sensors to maintain the set temperature.

Once the feed enters the column, the argon-nitrogen-helium mixture is purified by cryogenic distillation. The more volatile components, nitrogen and helium rise to the top of the column and are vented through the condenser, whereas the less volatile component, argon, flows down at the bottom of the column and is collected in the liquid phase in the reboiler. A 600W electric heater inside the reboiler will force the necessary boiling rate of the condensed argon to provide the desired reflux rate in the column. The reflux condenses in the condenser, and then flows down to the reboiler through the column. The purified argon is collected inside the reboiler, which is a custom made cylinder, 0.25 m in diameter and 0.38 m high for a volume of 18.00E-3 m^3. An electric heater on the output line is used to gasify the product out of the reboiler for storage.

The cooling power needed to cool down the gas, the column, the piping, and to keep the desired temperature profile inside the system is provided through a temperature-controlled cryocooler, model AL-600 from Cryomech, mounted on the top flange of the condenser. This cryocooler provides 600W of cooling power at 77K and it is coupled with a 600W heater and temperature sensors to maintain the set

temperature. The condenser is a custom made cylinder, 0.18 m in diameter and 0.11 m high for a volume of 2.75E-3 m^3. Nitrogen and helium are vented through the condenser.

The cryogenic distillation column, the reboiler, the condenser, and the cold piping are insulated by a vacuum jacket and insulated with twenty layers of super insulation, to reduce the heat loss for conduction and radiation.

Sampling lines are connected to a multi port Universal Gas Analyzer (UGA) from SRS to measure argon, nitrogen and helium contents of the inlet, outlet, and vent. The system is equipped with an instrumented gas panel that handles the flow of the gas through the various parts of the system. It includes a by-pass to further purify the product by sending it back in the column. A specific set of temperature probes and heaters monitor and control the temperature inside the whole system.

The system is equipped with a dedicated control system, fully automated and LabVIEW controlled (see Figure 2). The inlet composition may vary; the whole system has been designed to allow maximum flexibility during the operations.

The cryogenic distillation column is designed to purify the low radioactivity argon for the DarkSide-50 experiment. The cleanliness of the system and avoiding air contamination are extremely important.

All the piping is electropolished. Reboiler, condenser and condensing volume have been electropolished after fabrication. To minimize potential leaks, the connections are preferably welded. When welding was not possible, VCR connections have been used. The system has been helium leak checked at the level of 1.00E-8 mBar*l/sec to guarantee the leak tightness and an air-free system.

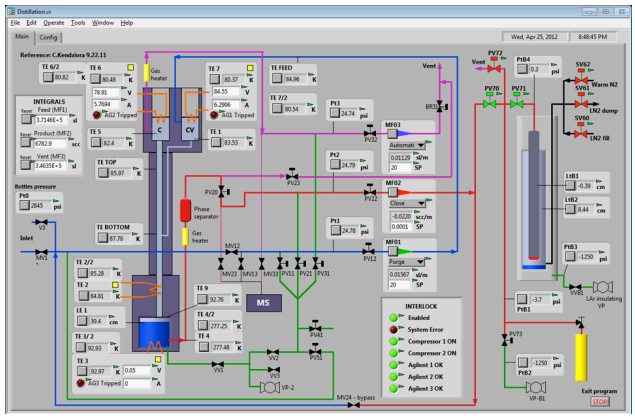

Figure 2 LabVIEW Control system GUI

OPERATIONS

We commissioned the cryogenic distillation plant with a known mixture of gas that is approximately the same as the output of the VPSA plant in Colorado (feed column in Table 1). This mixture was also used to calibrate the UGA: the ultimate sensitivity to nitrogen in argon is found to be ~500 ppm.

Table 1 Gas composition in the feed and in the product during continuous and batch modes

Component	Feed	Product Contin.	Product Batch
Argon	5%	99.9%	99.95%
Nitrogen	40%	1,000ppm	500ppm
Helium	55%	0	0

The cryogenic distillation column is designed to operate in a continuous distillation mode, where the gas to be separated is fed into the column continuously, while pure argon is collected in the reboiler, and nitrogen and helium are exhausted through the waste. However, if the conditions required for continuous flow operations do not result in adequate purity of the argon collected in the reboiler, the distillation column can be operated in a batch purification mode. In this mode, the input is turned off, and the liquid in the reboiler is further distilled with a retuned column temperature profile.

The distillation column was initially operated in the continuous flow mode. The temperatures of the distillation column were tuned to maximize the amount of argon collected, by minimizing the argon in the waste. At the same time, we wish to minimize the amount of nitrogen contamination in the reboiler.

Figure 3 shows the nitrogen-to-argon ratio of the product gas coming from the reboiler. The nitrogen concentration decreased continuously until the input feed gas supply was consumed. The final nitrogen concentration achieved in the continuous flow mode before the gas was consumed was ~1,000 ppm, giving 99.9% pure argon (Table 1). This value was confirmed by 2 independent measurements of a sample of the gas: Atlantic Analytical Laboratory

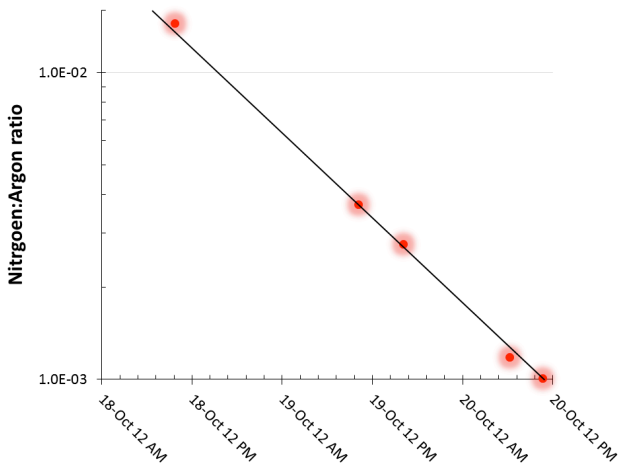

Figure 3 Nitrogen/Argon ratio as a function of time during continuous distillation

reported that the sample contained 700 ppm of nitrogen, and colleagues at Pacific Northwest National Laboratory measured the nitrogen content to be 920 ppm. The data from the UGA show that the nitrogen concentration was decreasing throughout the continuous distillation phase, and we are confident that continuous distillation can produce argon with a nitrogen contamination well below 1,000 ppm. Tests performed with different feed composition from those given in Table 1 showed that the operating parameters for the distillation column must be tuned for different input gas compositions in continuous mode.

We also tested the batch distillation technique. In this mode, the input stream is turned off, and the temperature gradient along the column was retuned to allow the excess nitrogen to escape the reboiler, while preserving the argon. The measured nitrogen concentration decreased until the nitrogen sensitivity limit of the UGA was reached. As mentioned, the lower limit of the UGA's sensitivity to measure the nitrogen concentration is ~500 ppm, which is equivalent to 99.95% pure argon (Table 1).

Figure 4 clearly shows the measured nitrogen concentration decreasing and plateauing at the nitrogen sensitivity limit of the UGA.

In addition to achieving high purity, it is important that a minimum of the argon in the feed gas be wasted. It is possible to estimate the amount of argon collected by two independent methods: from the liquid level recorded in the reboiler and from the integral of the mass flow meter. During the commissioning, the integrated efficiency for capturing the argon from the input gas mixture was between 72% and 83%. The discrepancy may be attributed to inaccurate calibrations of either the liquid level monitor or the mass flow controller. A small fraction of the product is consumed in the UGA for measuring the composition of the gas. We believe that in production mode we can increase the efficiency of argon collection to above 95%, due to the precise set of parameters that have been identified throughout the commissioning. We are also planning to couple the current UGA with a more sensitive unit. The measured production rate of argon with the current feed composition in continuous distillation mode is ~1 kg/day. If the feed gas contains more argon, or if the helium concentration is lower, the production rate of argon can be as high as 5 kg/day.

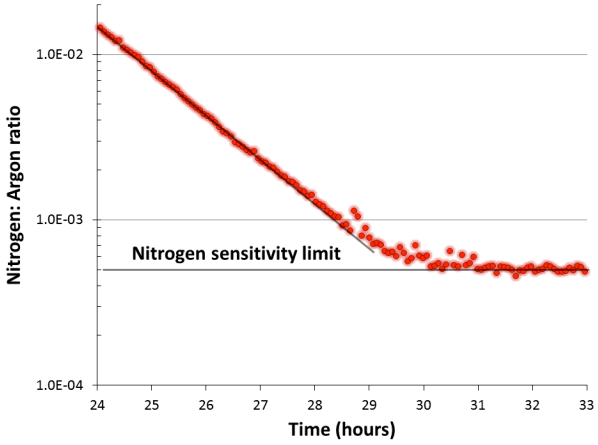

Figure 4 Nitrogen/Argon ratio as a function of time during batch distillation

CONCLUSIONS

In the first commissioning of the cryogenic distillation column at Fermilab, we have shown that this plant can effectively reduce the nitrogen content by more than 3 orders of magnitude and helium by more than 5 orders of magnitude. The argon produced by the distillation column contains less than 500 ppm of nitrogen, and the helium has effectively been eliminated. This argon purification was performed at a rate of about 1 kg/day with 76±5% collection efficiency. With the commissioning phase complete, we have now started to operate the distillation system to produce high-purity, low-radioactivity underground argon, which will be used for the DarkSide-50 experiment, scheduled to start operation in December 2012. We have purified 25 kg of argon to date.

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