Contract No:

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Argon Collection and Purification for Proliferation Detection

In order to determine whether a seismic event was a declared/undeclared underground nuclear weapon test, environmental samples must be taken and analyzed for signatures that are unique to a nuclear explosion. These signatures are either particles or gases. Particle samples are routinely taken and analyzed under the Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO) verification regime as well as by individual countries. Gas samples are analyzed for signature gases, especially radioactive xenon. Underground nuclear tests also produce radioactive argon, but that signature is not well monitored. A radioactive argon signature, along with other signatures, can more conclusively determine whether an event was a nuclear test. This project has developed capabilities for collecting and purifying argon samples for ultra-low-background proportional counting. SRNL has developed a continuous gas enrichment system that produces an output stream containing 97% argon from whole air using adsorbent separation technology (the flow diagram for the system is shown in the figure). The vacuum swing adsorption (VSA) enrichment system is easily scalable to produce ten liters or more of 97% argon within twelve hours. A gas chromatographic separation using a column of modified hydrogen mordenite molecular sieve has been developed that can further purify the sample to better than 99% purity after separation from the helium carrier gas. The combination of these concentration and purification systems has the capability of being used for a field-deployable system for collecting argon samples suitable for ultra-low-background proportional counting for detecting nuclear detonations under the On-Site Inspection program of the CTBTO verification regime. The technology also has applications for the bulk argon separation from air for industrial purposes such as the semi-conductor industry.

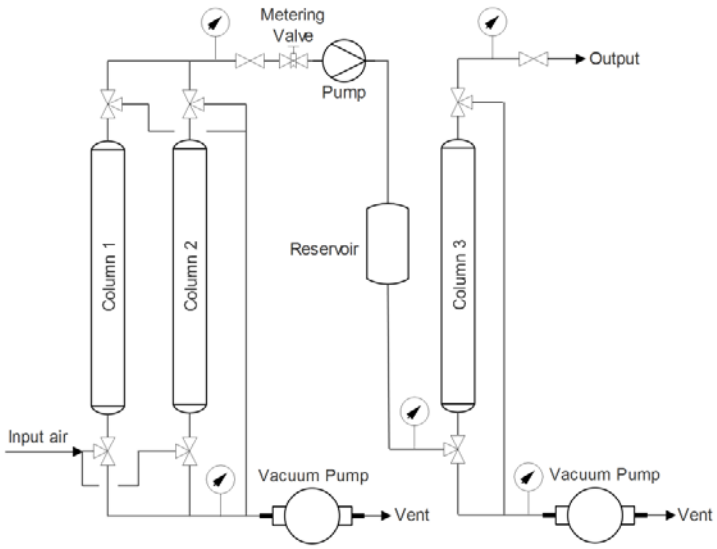

Figure 1: Flow diagram for VSA enrichment system

Awards and Recognition

None to date.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature	**Date**

Argon Collection and Purification for Proliferation Detection

Project Team: Randall Achey (Primary), Douglas Hunter

Subcontractor: None

Thrust Area: Non-Proliferation & Nuclear Deterrent

Project Type: Standard

Project Start Date: October 1, 2014
Project End Date: September 30, 2015

SRNL has developed a continuous gas enrichment system that produces an output stream containing 97% argon from whole air using adsorbent separation technology. The vacuum swing adsorption (VSA) enrichment system is easily scalable to deliver ten liters or more of argon within twelve hours. Testing has shown that gas chromatographic separation using a column of modified hydrogen mordenite molecular sieve is capable of further purifying the sample to better than 99% purity after separation from the helium carrier gas. The combination of these concentration and purification systems has the capability of being used for a field-deployable system for collecting argon samples suitable for ultra-low-background proportional counting for detecting declared/undeclared underground nuclear detonations under the On-Site Inspection program of the Comprehensive Test-Ban-Treaty Organization verification regime.

FY2015 Objectives

- Develop a VSA argon enrichment system that outputs 10 L of 97% pure argon within 12 hours from a whole air input without the use of cryogenics or refrigeration.
- Develop a gas chromatographic purification step that purifies the output of the VSA system to 99.99% argon.

Introduction

In order to determine whether a seismic event was a declared/undeclared underground nuclear weapon test, environmental samples must be taken and analyzed for signatures that are unique to a nuclear explosion.[1] Gas samples are analyzed for signature gases, especially radioactive xenon. Underground nuclear tests also produce radioactive argon, but that signature is not well monitored.[2] The high-energy neutron flux produced by underground nuclear detonations can convert ^{40}Ca in the soil into ^{37}Ar by capture of a neutron and emission of an alpha particle.

The quantity of ^{37}Ar that is produced by an underground nuclear detonation greatly exceeds the amount that is naturally occurring.[3] ^{37}Ar has a half-life of 35 days, allowing detection of emissions produced by an underground nuclear detonation weeks after it occurs. Because the longest half-life of the xenon isotopes produced by a nuclear explosion is 11 days for ^{131m}Xe, ^{37}Ar gives the opportunity to detect the signature of a nuclear explosion for a longer time after the event. Despite efforts to contain the products of the detonation, ^{37}Ar eventually escapes into the atmosphere because its formation is in the overburden surrounding an underground nuclear test.[3] Even if there is no immediate venting of the explosion products, variation in atmospheric pressure due to weather fronts will draw the gases up from the ground, a process known as barometric pumping.[4] Collection of large samples of argon from the atmosphere, along with ultra-low-background proportional counting techniques, can detect the ^{37}Ar even at long distance. A ^{37}Ar signature along with other signatures can more conclusively determine whether an event was a nuclear test.

Approach

An argon concentration system using VSA was developed for the initial separation of argon from whole air. The system passes air over a bed of molecular sieve that adsorbs the major components of air while allowing argon to pass through. The molecular sieve has been modified to reduce the pore size. The tailoring of the pore size enables a size exclusion separation, inhibiting noble gases from entering the pores while still letting nitrogen and oxygen enter the pores. This step performs the majority of the separation necessary, producing an output that is 97% argon. For further purification, a separation using a gas chromatographic column was explored. This step removes most of the remaining impurities from the argon to produce, after separation of the argon from the helium carrier stream, an output with purity better than 99%.

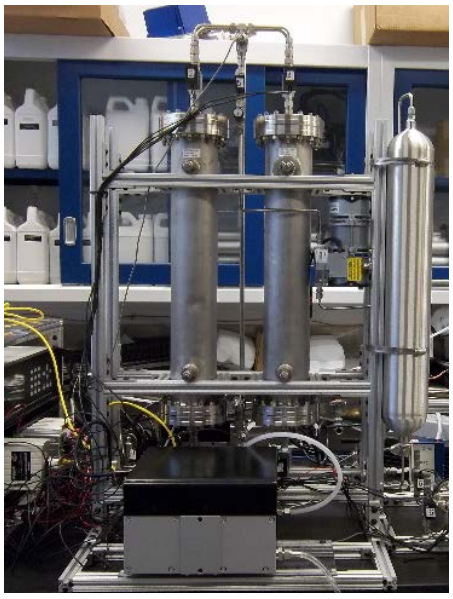

Figure 1. Example benchtop VSA system for argon enrichment

Results/Discussion

A benchtop VSA enrichment system was assembled and tested, shown in Fig. 1. Figure 2 shows the flow diagram for the VSA system. Dry input air at a flow of 20 L/min is fed into a canister filled with modified sodium mordenite molecular sieve zeolite. Nitrogen and oxygen are preferentially adsorbed by the molecular sieve, allowing a stream enriched in argon to flow from the output of the canister. Before nitrogen and oxygen start to pass through the bed in high concentration, the flow is stopped and the argon-enriched gas in the output manifold is pumped into a holding reservoir.

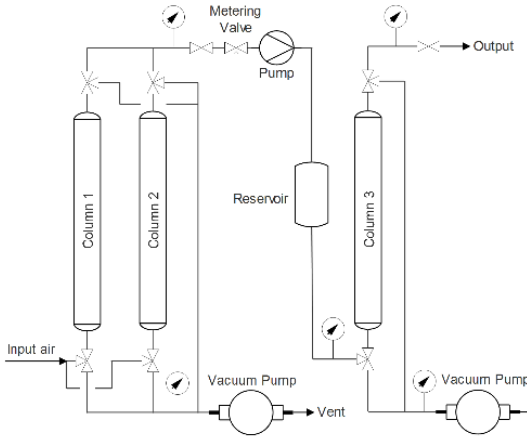

Figure 2: Flow diagram for VSA system for argon enrichment

After one canister is saturated, the input flow is switched to the other canister and the saturated canister is regenerated under vacuum. Production is alternated back and forth between the pair of canisters to provide a continuous output of gas enriched in argon. The output of the first enrichment stage is fed from the reservoir into a second enrichment stage consisting of a canister filled with the same molecular sieve. This canister is a special design to improve efficiency of concentration. The input flow to the second enrichment stage is started when the pressure in the holding reservoir reaches a set level. The output of the second VSA enrichment stage at 97% argon is 5 L in 12 hours. If the VSA system is run with an output of 90% argon, then the system developed

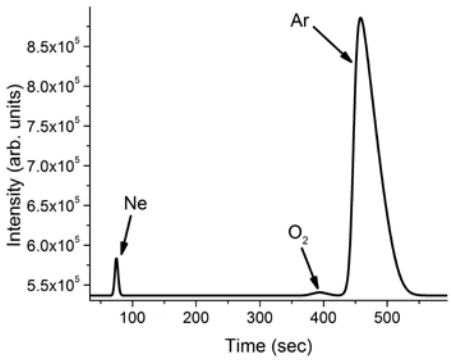

Figure 3. Chromatogram of VSA output for residual contamination assessment

outputs over 10 L of argon in 12 hours and no scale up of the VSA system is necessary.

A gas chromatographic column was tested for purification of the VSA output. It was found that a column packed with modified hydrogen mordenite performs well for separating argon from the residual impurities, producing an output with purity better than 99% when separated from the helium carrier gas. A chromatogram of the column output is shown in Fig. 3. In the chromatographic purification step, the output of the VSA is flowed over a column filled with modified hydrogen mordenite. Pulses of input gas are interspersed and the argon peaks are routed to the final output sample, while the other peaks are discarded. A column containing molecular sieve could be sized appropriately to purify 10 L of argon in 12 hours. The chromatographic separation can easily handle 90% argon in the input with 10% impurities, which would allow use of the VSA system on the scale developed and no scaleup of the VSA would be necessary for a full-size system.

FY2015 Accomplishments

- Developed a VSA system that produces 5 L of 97% argon in 12 hours continuously from whole air without the use of cryogenics. The system is easily scalable to provide 10 L of argon in 12 hours.
- Developed a chromatographic separation that can remove most of the residual impurities, scalable to handle necessary production rate.

Future Directions

- Integrate the argon concentration steps into a benchtop demonstration system and perform testing and optimization of the complete system.
- Implement final separation of the argon from the helium carrier stream of the gas chromatographic separation step using adsorption on activated charcoal (a widely-used separation technique).
- Obtain customer funding for development of field-deployable argon collection system.

FY 2015 Publications/Presentations

1. Mid-year review presentation, February 2015

References

1. Schulze, J.; Auer, M.; Werzi, R. Appl. Rad. and Isot. 2000, 53, 23.
2. Aalseth, C.E.; Day, A.R.; Haas, D.A.; Hoppe, E.W.; Hyronimus, B.J.; Keillor, M.E.; Mace, E.K.; Orrell, J.L.; Seifert, A.; Woods, V.T. Nucl. Inst. and Meth. in Phys. Res. A 2011, 652, 58.
3. Haas, D.A.; Orrell, J.L.; Bowyer, T.W.; McIntyre, J.I.; Miley, H.S.; Aalseth, C.E.; Hayes, J.C. "The Science Case for ^{37}Ar as a Monitor for Underground Nuclear Explosions", Report No. PNNL-19458, 2010.

4. Carrigan, C.R.; Heinle, R.A.; Hudson, G.M.; Nitao, J.J.; Zucca, J.J. "Barometric Gas Transport Along Faults and Its Application to Nuclear Test-Ban Monitoring", Report No. UCRL-JC-127585, 1997.

Acronyms

CTBT: Comprehensive Nuclear-Test-Ban Treaty
CTBTO: Comprehensive Nuclear-Test-Ban Treaty Organization
VSA: Vacuum Swing Adsorption

Intellectual Property

Invention disclosure will be submitted for the non-cryogenic generation of argon from air and its application.

Total Number of Post-Doctoral Researchers

None.