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Test Operation of a Prototype,
Solid-State, Helium Purification Cell

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**Test Operation of a Prototype,
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R. A. Clark
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TEST OPERATION OF A PROTOTYPE,
SOLID-STATE, HELIUM PURIFICATION CELL

by

R. A. Clark*, B. J. Melton**, C. R. Winkelman

ABSTRACT

Two solid-state helium diffusers were tested and their performance was determined under thermal conditions, radiation exposure, and pressure gradients typical of a reactor cover-gas purification system. Essentially complete removal of impurities Ar, N₂, O₂, CH₄, H₂O, Xe, and Kr from helium in a single pass through the diffusers was demonstrated. At operating temperatures above 400°C, H₂ was detected in helium delivered by the diffusers. Measurements were made of helium flow rates through the diffusers at temperatures from 250 to 500°C, and the diffusion constant was determined.

The diffusers successfully operated for several hundred hours at maximum temperature without cooling to the tube bundle seal and with mechanical vibration of the diffuser at the seal flange. Test operation showed that the diffusers could be successfully used in a helium purification system requiring high purity, simple and remote operation, and little maintenance. Recommendations are made for improvement of the quality and capacity of a diffuser.

INTRODUCTION

Fast breeder reactors that use sodium for the primary and secondary coolant will require a high-purity cover gas to protect the coolant from contamination. Helium, with its low density, inertness to ordinary chemical reactions, and absence of neutron activation, has been selected as the cover gas for several fast breeder reactors.¹⁻³ Because high-purity helium is required, provisions must be made to control the quantity of fission-product gases, Xe and Kr; contaminant gases, H₂, CO, CO₂, H₂O, CH₄, N₂, and Ar; and organic vapors. Contaminant control methods⁴⁻⁹ currently in use in helium-cooled reactors require a complex system of low-temperature condensers and adsorption beds, hot CuO beds, molecular sieve columns, filters,

and compressors. Purification systems for cover gas in sodium-cooled reactors are less elaborate than in helium-cooled ones, but involve similar chemical reactions and equipment.^{10,11}

Many of the problems of chemical purification--regeneration, recharging, or replacement of reactants and low-temperature condensers and associated refrigeration systems--can be eliminated by separating the impurities from helium in a solid-state diffuser.

In solid-state diffusion, the diffusion rates of atoms, molecules, or ions in a solid lattice differ. Density of the solid lattice causes strong interactions between diffusing entities and the atoms or ions of the solid lattice. The rate of transport of a diffusing species within the solid is directly related to the nature of the interaction. In some cases the diffusion occurs by atomic jumps from one interstitial site to another as a result of thermal agitation of the solid and the solute.

*Present address: U. S. Atomic Energy Commission, Division of Licensing and Regulations, Washington, D. C.

**Present address: U. S. Atomic Energy Commission, Richland Operations Office, Richland, Washington.

In other cases diffusion occurs because the diffusing species substitutes for one of the atoms of the solid. In either case the diffusing entity must receive enough energy to surmount a potential barrier caused by the force fields of the neighboring atoms. Experiments have shown that solid-state diffusion rates of atoms with the same atomic weight vary by factors of as much as a million or more. Specific substitution interactions permit essentially complete separation in a single diffusion stage.¹²

Investigators have measured the diffusion of helium through silica glass^{13,14} (quartz), and several proposals have been made for using silica-glass diffusers to separate helium from natural gas and to purify helium for laboratory use.^{10,15,16} Proposals have been made for using silica-glass diffusers in reactor systems,¹⁷ but no pilot-plant tests of the diffuser have been conducted.

The objective of this investigation is to establish the performance of a prototype, solid-state, silica-glass diffuser under (1) thermal conditions, (2) radiation exposure, and (3) pressure gradients typical for a cover-gas purification system. In addition, the performance of the diffuser under adverse conditions (mechanical vibration and loss of coolant to the tube bundle seal) is reported.

EQUIPMENT

Diffuser

In the two solid-state diffusers tested, a silica-glass membrane is used to separate helium from its contaminants. The glass, in the form of small capillary tubes, has good chemical and mechanical stability, which allows it to operate at high temperatures and differential pressures. Diffusion of gas through a tubular glass membrane is described by the equation

$$\frac{dq}{dt} = \frac{KA\Delta p}{w} = \frac{K\pi DL\Delta p}{w}, \quad (1)$$

where

$\frac{dq}{dt}$ = gas flow rate, cc/sec at STP

K = permeability constant of the gas at temperature T, cm²/sec

A = surface area of the glass, cm²

D = tubing diameter, cm

L = tubing length, cm

w = tubing wall thickness, cm

Δp = pressure difference across the wall, atm.

As shown by Eq. (1), flow rate is proportional to D/w, which permits a useful diffuser to be made by assembling a large number of very small tubes into a single shell.

The diffusers tested were manufactured by Electron Technology, Inc., Kearny, New Jersey. The diffuser shown schematically in Fig. 1 is typical of the two tested. Principal components are the (1) stainless steel shell, (2) silica-glass tubes, (3) tube bundle seal, and (4) cooling water jacket. The diffuser shell, flanges, and outlet plenum are Type 304 stainless steel. Shell design temperature and pressure were 400°C and 1000 psi, respectively. Silica-glass tubes 0.01-in. o.d., with a diameter-to-wall thickness ratio (D/w) of 6, provide a large surface area and adequate channels for conducting purified helium to the outlet plenum. Figure 2 shows an enlargement of a section through silica-glass tubing in the epoxy seal.

The first diffuser tested had 3000 silica-glass tubes with an active length of 4-1/2 feet. The tube bundle seal was made by passing the tube bundle through a stainless steel ferrule and potting with an epoxy. The ferrule had been welded to a flange for sealing between shell and outlet flanges with "O" rings. Figure 3 shows the metal ferrule design and Fig. 4 is a photograph of the complete diffuser.

The second diffuser had 500 silica-glass tubes with an active length of 4-1/2 feet. The tube bundle seal was made by potting the tubes in an epoxy ferrule and flange, which was sealed with "O" rings between shell and outlet flanges. Figure 5 is a photograph of the all-epoxy tube bundle seal.

Salt Bath

That portion of the diffuser below the mounting flange was suspended in a molten salt bath for temperature control. The molten salt container was a Type 304 stainless steel tube 3-in. o.d. x 1/4-in. wall x 10 ft long. Tubular resistance heaters were attached outside the container, and heater power was supplied by a manually operated adjustable auto-transformer. Three inches of insulation were installed over the heaters. A flange at the top of the container mated with the diffuser mounting flange. DuPont HiTec heat-transfer salt was used

Fig. 1. Silica-glass diffuser.

for the salt bath. Readings of thermocouples attached to the immersed length of the diffuser varied by no more than $\pm 3^\circ\text{C}$ after temperature equilibrium had been reached.

Gas Chromatograph

A Beckman Model GC-2A gas chromatograph analyzed helium input. Two chromatograph columns were used: a primary molecular sieve column and a silica gel column for measuring CO and CO₂ if required. A series of test runs established 100°C as the column temperature that provided the best resolution with a detector current of 380 mA. All analysis was done at this temperature and current. The reference gas used throughout calibration and routine operation of the chromatograph was Bureau of Mines analytical grade helium.

The chromatograph was calibrated with blends of analytical grade helium and other gases as shown in Table I.

Fig. 2. Silica-glass tubing in epoxy seal.

Fig. 3. Stainless steel ferrule and epoxy tube bundle seal.

Fig. 4. Silica-glass diffuser assembly.

Fig. 5. Epoxy tube bundle seal.

TABLE I

Calibration Gas Standards			
Impurity Impurity	Std No. 1 (ppm)	Std No. 2 (ppm)	Std No. 3 (ppm)
H ₂		36	62
O ₂	1.0	8	
N ₂	5.78	30	62
Kr	10.0	36	
Xe	11.9	36	
Ar			62
CH ₄			62
Ne	7.2		

Using the standards of Table I, the sensitivity and limit of detection of impurities were established, as shown in Table II.

TABLE II

Calibration of Beckman Gas Chromatograph

Impurity	Concentration (ppm)	Sensitivity (ppm/div)	Detectability Limit (ppm)
H ₂	36	13.7	3.4
O ₂	8	1.1	0.5
N ₂	30	1.7	0.5
Kr	36	2.1	0.5
Xe	36	7.0	1.7
Ar	62	1.5	0.5
CH ₄	62	3.9	0.9
Ne	8	1.2	0.5

Two possibilities exist for ambiguity with the combination of impurities and chromatograph columns: hydrogen and neon, and oxygen and argon. This ambiguity was resolved by using a CEC-26-611 mass spectrometer (modified for use in this sensitivity range) to identify the components.

Output from the gas chromatograph was monitored and recorded on a single pen, 0-1 mV Honeywell recorder.

Thermocouples

The diffuser shell surface temperature was measured by 1/8-in. sheathed, Chromel-Alumel thermocouples fastened at 2 in., 13-1/2 in., and 27-1/2 in. above the diffuser inlet fitting. These thermocouples were calibrated prior to installation in a standard melting-point apparatus using zinc and tin as reference materials. Unclad Chromel-Alumel thermocouples measured the seal flange and salt-bath container surface temperatures.

The output from each thermocouple was indicated and recorded on a 0 to 1000°C multipoint Honeywell recorder.

Leak Detector

A mass spectrometer, Atlas Gasdetektor, was used to test integrity of all diffusers using argon. The spectrometer, calibrated with an argon standard leak, demonstrated a sensitivity of 1×10^{-11} atm cc/sec.

Pressure Gauge

A calibrated Heise pressure gauge (12-in. face, 0 to 3000 psi range) read helium pressure at the helium inlet.

TEST DESCRIPTIONS

Leak Tests

Following gamma irradiation of the seal, the diffuser was mounted at the support flange and leak tested. The shell (inlet) side of the diffuser was pressurized to 150 psig with argon. The diffuser outlet was evacuated to 10^{-6} torr and was monitored for argon leakage with the mass spectrometer for several hours.

Performance Tests

Diffuser performance was determined by measuring helium flow rate through the diffuser and by monitoring the diffuser output with the gas chromatograph. After leak testing, the diffusers were mounted in the salt bath. Diffuser input was connected to the inlet manifold, which allowed the introduction of helium or the various helium blends containing gaseous impurities. Diffuser output flowed through the gas chromatograph and then was discharged to the atmosphere. The diffuser and associated test equipment is shown in Fig. 6.

An operating temperature was established by manually setting the salt-bath power supply and allowing the bath to come to equilibrium (~ 24 hr). Inlet pressure was adjusted to 165 psi, and helium flow rate through the diffuser was measured by collecting the helium over water in a graduated cylinder while measuring collection time with a stop watch. Samples (5 cc) were taken periodically from the diffuser output and analyzed in the chromatograph. Although thermal equilibrium was reached in approximately 24 hr, operation of the diffuser

Fig. 6. Test apparatus.

at each test temperature was continued for an additional 48 hr. Flow rates were measured twice daily, and at least 6 samples of the output were analyzed each day.

Irradiation Tests

Screening tests on several compounds suggested by the diffuser manufacturer for use in the tube bundle seals were conducted on cylindrical samples 1-1/2-in. o.d. by 1-1/2 in. long. A 1/2-in.-diam hole was drilled through the center of each sample to accept a ^{60}Co source. Before insertion of the source, all dimensions and the general appearance of the samples were noted. The source was then inserted in the central hole and allowed to remain until the sample had obtained the desired exposure. At the end of exposure the source was removed and samples underwent an examination for any changes in dimensions or appearance.

The tube bundle seal was exposed to ^{60}Co irradiation by placing the source 6 in. from the seal for a time necessary to achieve the desired exposure. Performance of the diffuser and tube bundle seal was determined before and after irradiation as explained in Performance Tests.

Thermal and Mechanical Tests

After the performance tests had been completed at the maximum operating temperature ($\sim 495^\circ\text{C}$ for 3000-tube diffuser and $\sim 445^\circ\text{C}$ for the 500-tube diffuser), water to the cooling water jacket was turned off and the tube bundle seal was allowed to operate without cooling. Performance of the diffuser and tube bundle seal was determined as explained in Performance Tests. Each diffuser was allowed to operate for 168 hr without cooling water. A 60 cycle/sec vibrator was then mounted on the seal flange and vibrated for an additional 120 hr in the test of the 3000-tube diffuser and 385 hr in the test of the 500 tube diffuser. Total time without coolant was 288 and 553 hr for the 3000- and 500-tube diffusers, respectively. Performance was again monitored.

TEST RESULTS

The diffusers tested had starting leak rates of less than 1×10^{-10} atm cc/sec of argon; however, both the 3000- and 500-tube diffusers developed leaks in the tubing. Leaks in the 3000-tube unit occurred during the performance test conducted after irradiation of the seal. Appearance of contaminants (H_2 , Ar, N_2 , and CH_4) in diffuser output was the first indication of leakage. The diffuser was cooled to room temperature, and an argon mass spectrograph leak test was attempted. Leakage was so great that the outlet plenum could not be evacuated. The unit was shipped to the manufacturer for repairs and 5 tubes were found to leak. Leaks were repaired by fusing outlet tips of the tubes (equivalent to "plugging a tube" in a shell and tube heat exchanger). Upon return from the manufacturer, the unit was again leak tested and was found to have a leak in the seal region ($\sim 7.8 \times 10^{-7}$ atm cc/sec argon). Although this exceeded the desirable leak rate, the unit was mounted in the salt bath to perform the thermal test. The leakage disappeared as soon as the unit was brought up to temperature and was not detected during the remainder of the test operation.

The 500-tube diffuser began leaking during the first few hours of the performance test. Leakage was detected by a sudden increase in helium flow rate. Inspection revealed two leaking tubes, which were sealed off by fusing the tip. The diffuser was reinstalled in the salt bath to continue the

performance test, and leakage was again detected by an increase in flow rate. One additional tube was leaking and was repaired by fusing the tip. After repairs no leakage was detected during the remainder of testing.

The ability of the diffusers to separate contaminants from helium was successfully demonstrated. Input helium containing, Xe, Kr, N₂, O₂, H₂, Ar, CH₄, and H₂O was used and all impurities except H₂ were removed to a level below the limits of detectability (see Table II). Hydrogen was generally detected at diffuser temperatures greater than 390°C. Since the partial pressure of the hydrogen in the diffuser cell was not measured, only qualitative information was obtained on the passage of hydrogen through the silica glass.

Performance of the diffusers in terms of helium flow rate versus operating temperature is shown in Fig. 7. Helium flow rate in both the 3000- and 500-tube diffuser was slightly higher (~ 20%) than predicted from manufacturer's data. This is probably due to the use of the salt bath, which preheated inlet helium to the diffuser temperature before it entered the shell. The diffusion constant, K, was calculated from the flow-rate data and Eq. (1), and is shown in Fig. 8.

Irradiation tests on three sealing compounds (Hysol C8-4142 Epoxy, with Bakelite ERL-2807 hardener; Hysol C8-4142 Epoxy, with Hysol H4-3410 hardener; and Dow Corning 850 RTU silastic, with 850 catalyst) demonstrated resistance to radiation damage. There were no dimensional changes or observable deterioration after an exposure of 9×10^7 r. This exposure was chosen as being equivalent to ~ 30 years of seal operation in a typical cover-gas purification system of a 20-MW sodium-cooled fast reactor.

In the 3000-tube diffuser the epoxy sealant (Hysol C8-4142 Epoxy plus Hysol H4-3410 hardener plus silica-glass filler) was irradiated to an exposure of 3×10^7 r. Mass spectrometer leak tests and performance tests following this exposure showed no change in the tube bundle seal.

The ability of the diffuser to operate successfully for many hours following a loss of coolant to the seal was demonstrated. The 3000-tube diffuser operated for 288 hr and the 500-tube diffuser for 553 hr without cooling. A maximum seal flange surface temperature of 48°C for the 3000-tube diffuser

Fig. 7. Diffuser temperature versus helium flow rate.

Fig. 8. Diffuser temperature versus diffusion constant (K).

and 57°C for the 500-tube diffuser were measured. Actual seal temperature could not be measured, but in both diffusers the shell side of the seal was exposed to shell-side helium, which would approach the diffuser operating temperature (495° and 445°C). No change in the integrity of the seal or the performance of the diffuser was observed during this test.

Each of the diffusers was subjected to mechanical vibration (60 cycles/sec) at the tube bundle seal flanges for at least 120 hr while at their maximum operating temperature and with no seal coolant flow. Although the amplitude of the vibration was not measured, an observable motion was imparted to the diffuser. The performance of the diffuser was not changed by the vibration and the tube bundle seal maintained its integrity.

CONCLUSIONS AND RECOMMENDATIONS

Test operation of the prototype, silica-glass diffusers, under conditions similar to those which might exist in a reactor cover-gas purification system, has established the following:

1. Ability of the diffuser to separate helium from all gaseous impurities except hydrogen in a single pass.
2. Acceptability of the epoxy tube bundle seal for the conditions of testing.
3. Simplicity of operation.
4. Ease of maintenance.
5. Ability of the diffuser to operate without cooling the tube bundle seal.
6. Ability of the diffuser to withstand mechanical vibration.
7. The diffusion constant (K) for use in design of larger diffusers.
8. Acceptability of the heat-transfer salt as a method of maintaining the diffuser at operating temperature.
9. Feasibility of using the diffuser as a method of concentrating low-level impurities for high sensitivity impurity measurement.

Although present technology would permit the diffusers to be used in helium systems requiring relatively low flow rates (0.4 cfm STP) certain improvements and developments will be necessary before diffusers for use in higher flow-rate systems

can be built. It is recommended that:

1. Manufacture and quality control of the silica-glass tubing be improved to provide tubing that is round, has a uniform wall thickness, a $D/w > 6$, is free from inclusions, and is available in 30-ft lengths.
2. Seal development be continued to establish the maximum number of tubes that may be used with present sealing compounds and technology; and that new tube bundle sealing methods be investigated.
3. Diffuser design incorporate features that will allow field sealing of the outlet ends of leaking tubes.
4. Quality control by the manufacturer include leak testing of the diffuser after it has been heated to operating temperature.
5. Present water jacket cooling of the tube bundle seal be replaced by fins or other extended surfaces to provide atmospheric cooling of the seal.

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REFERENCES

1. J. M. Davidson and L. M. Finch, "Progress Report Fast Flux Test Facility, Interim Reference Concept," Report BNWL CC 400, Battelle Northwest Laboratory, February 1, 1966.
2. Directory of Nuclear Reactors, Vol. IV: Power Reactors, IAEA, Vienna, 1962.
3. "Feasibility Study of a 1000 MWe sodium-cooled Fast Reactor," Report NAA-SR-11378, Atomic International, July 1966.
4. "Final Hazard Summary Report Peach Bottom Atomic Power Station," Report NP-9115, Part C, Vols. 1 through 5, 1963.
5. H. de Bruijn, A. Gruetter, E. Roemberg, and F. C. Wood, "Removal of Fission Product Noble Gases from the Helium of a High-Temperature Gas Cooled Reactor Using Charcoal at Low Temperatures," Report DP-Report-258, UKAEA, January 1964.
6. "Ultra High Temperature Reactor Experiment (UHTREX) Hazard Report," Report LA-2689, Los Alamos Scientific Laboratory, March 1962.
7. "Design Study Report for TARGET," Report GA-4706, General Atomics, March 9, 1964.
8. "Purification Plant," Technical Description AVR-Nuclear Power Plant, File Code: H 2-C 4, Brown Boveri/Krupp, February 25, 1963.

9. C. D. Scott, "Removal of Hydrogen, Carbon Monoxide and Methane from Gas Cooled Reactor Coolants," Report ORNL-TM-20, Oak Ridge National Laboratory, November 1961.
10. "Hazard Summary Report EBR II," Report ANL-5719 (Addendum), Argonne National Laboratory, June 1962.
11. "Enrico Fermi Atomic Power Plant," Report APDA-124, Atomic Power Development Associates, January 1959.
12. K. B. McAfee, Jr., "Diffusion Separation," Encyclopedia of Chemical Technology, 2d Suppl., Interscience Publishers, New York, 1960, pp. 297-315.
13. V. O. Altemose, "Gas Permeation Through Glass," Proceedings of the Seventh Symposium on The Art of Glass Blowing, 1962.
14. V. O. Altemose, "Helium Diffusion Through Glass," J. Appl. Phys. 32, 1309 (1961).
15. K. B. McAfee, Jr., "Helium and Diffusion Separation," Bell Laboratories Records, October 1961, pp. 354-58.
16. N. Melnyk and H. W. Habgood, "Extraction of Helium from Natural Gas. The Diffusion-Through-Glass Process," Transactions Annual Meeting Petroleum and Natural Gas Division, Vol. LXIV, 1961, pp. 463-69.
17. "Progress Report on Pebble Bed Reactor Program for the Period June 1, 1959 to October 31, 1960," Report NYO-9071, Sanderson and Porter, New York, November 1960.