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**UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
HELIUM ACTIVITY
HELIUM RESEARCH CENTER
INTERNAL REPORT**

EVALUATION OF HELIUM PURIFICATION

BY A LABORATORY QUARTZ DIFFUSION CELL

BY

S. E. Churchwell

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PROJECT NO. 5573

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Work on this project completed September 1966.

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ABSTRACT

A commercially available laboratory model helium purifier which operates on the principle of preferential diffusion of helium through quartz tubes was evaluated to determine the purity of the effluent helium. Analysis of the effluent helium from the purifier showed that its utility was limited because of an anomalous evolution of hydrogen and the significant diffusion of neon through the quartz tubes.

INTRODUCTION

The preferential diffusion of helium through quartz has been the subject of scientific study for over 40 years, and there is an extensive body of literature on the subject. In 1958, Kohman and McAfee (2)^{2/}

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^{2/} Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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of the Bell Telephone Laboratories, New York, N.Y., reported the development of a laboratory-scale helium purifier based on the preferential diffusion of helium through quartz capillary tubes.

About 1960 there was an unsuccessful attempt at the Helium Research Center to build a small helium purifier containing quartz capillary tubes. Later, two major companies, M. W. Kellogg Company, New York, N.Y., and the General Engineering Laboratory of General Electric, Syracuse, N.Y., proposed joint development with the Helium Activity of a process for plant-scale separation of helium from other gases by diffusion through large bundles of quartz tubes. Both proposals were rejected as impractical by the Helium Activity.

It was not until a laboratory purifier built by Electron Technology, Inc., Kearny, N.J., became commercially available in 1964 that interest in this mode of helium purification was revived at the Helium Research Center. The introduction and extensive marketing of this laboratory model helium purifier, which is based on preferential diffusion of helium through quartz tubes, created considerable interest at the Center.

This renewed interest was due to both economic and theoretical considerations. Such a purifier might simplify, if not eliminate, extensive efforts to obtain purified helium for research and other uses. For example, it might replace the presently used liquid-nitrogen-cooled adsorbent traps to purify helium carrier gas in chromatographs. Also, many users of helium contact the Helium Activity regarding the effectiveness of equipment such as the diffusion cell herein discussed.

Because of these considerations, one of the multitubed quartz diffusion cells was purchased for evaluation and possible use. The purpose of this report is to give the results of the evaluation.

LOCAL HISTORY OF CELL

A brief history of this purifier exemplifies the general experience that may be expected during the use of similar cells. The unit, initially received with broken tubes, was returned to the manufacturer for repair. After the purifier was returned to the Helium Research Center, vacuum pump oil inadvertently entered the jacket around the quartz tubes during one of the necessary evaluation procedures. Tube breakage was experienced, either because of the oil on the tubes or because of an attempt to clean the tubes, requiring return to the factory for a third set of tubes. During use with the first cylinder of helium after this repair, a powdered iron compound from within the cylinder entered the cell. This material adhered to the walls of the quartz tubing, causing tube embrittlement and breakage. The purifier was again returned to the factory for installation of a fourth set of tubes. Upon return from the factory, the remainder of the evaluation tests were completed while using particulate filters in the inlet gas line to the cell.

Figure 1 is a photograph of the in-line filter, showing the

Figure 1.-In-line filter, showing black iron powder and brass turnings.



FIGURE 1.— In-Line Filter, Showing Black Iron Powder
and Brass Turnings. (3.5 X)

black iron material and brass turnings found after the helium from the first cylinder had passed through the filter. Because of filter paper breakage, as shown in figure 1, subsequent filtering was achieved by using commercial cupped and fritted metal filters with 5- to 10-micron pore sizes. Deposition of these materials from only one cylinder may have been a chance occurrence; no deposits were found after removal of other filters.

TEST RESULTS USING THIRD SET OF TUBES

Prior to the failure of the third set of tubes, the cell outlet (purified helium) was connected directly to a mass spectrometer where analyses by a sensitive high pressure method (6) could be made. Table 1 shows the results of the analyses made on the effluent helium from the diffusion cell. The analyses given for the supply helium, however, were determined by the Bureau of Mines freeze-out procedure (1). Significantly, table 1 gives data representing one method of analysis (6) while data given later are based on a different method (1). Table 1 also shows, in addition to the expected low values obtained for nitrogen, surprisingly high hydrogen and neon contents in the purified gas.

TEST RESULTS USING FOURTH SET OF TUBES

Analyses by the high pressure method (6) were abandoned because of limited access to the mass spectrometer and air leakage problems associated with coupling and decoupling the two instruments. After

TABLE 1.-High pressure mass spectrometer results of analyses on effluent helium from diffusion cell using third set of quartz tubes

Cell oper time, hrs	MS run no	Cell oper temp, °C	Cell inlet press, psig	Analysis, ppm							Total, less H ₂ O
				H ₂	Ne	O ₂	N ₂	CH ₄	Ar	CO ₂	
Supply helium	(J197471)	to cell		<u>1/0</u>	<u>1/12.9</u>	<u>1/8.7</u>	<u>1/75.0</u>	<u>1/0</u>	<u>1/0.9</u>	<u>1/0.4</u>	<u>1/97.9</u>
23	1,652	335	1,000	7.2	2.8	2.1	4.4	0	<.1	<.1	16.7
25	1,653	335	1,000	7.2	2.3	2.0	3.9	0	<.1	<.1	15.6
283	1,661	335	400	55.1	32.8	4.7	6.9	0	.1	.1	99.7
284	1,662	335	400	54.1	31.8	3.6	5.5	0	<.1	<.1	95.2

1/ Value determined by freeze-out procedure (1).

the fourth set of tubes was factory-installed, samples were analyzed by the freeze-out procedure (1), either by direct sampling from the purifier or by collecting the purified gas in properly prepared sampling containers termed "composite samples." The results are shown chronologically in table 2. The column headed "Cell oper time" in both tables 1 and 2 refers to the cumulative operating time of the tube set involved since receipt at the Helium Research Center. Sample numbers RT-1460, -1467, and -1523 are assumed to have been contaminated by air from sources other than the purifier. Sample numbers RT-1458 and -1497 also showed external air contamination that probably resulted from a failure to meet the critical flowrate requirements of the analytical freeze-out procedure (1). (The purifier could not furnish an adequate volume of helium for proper operation of the freeze-out apparatus.) Analyses of all the air-contaminated samples are included in table 2 to support the conclusions regarding other impurities.

ANOMALOUS HYDROGEN EVOLUTION

Both tables 1 and 2 show the presence of hydrogen in the purified helium effluent from the diffusion cell. The presence of hydrogen is termed an anomaly because there was not any detectable hydrogen in the analyzed helium supplied to the cell. A calculation revealed that the fourth set of tubes in the cell mysteriously produced over $50 \text{ cm}^3\text{-atm}$ of hydrogen during the course of the tests. It is not known whether the hydrogen was occluded residually in the quartz pores or produced by some chemical reaction.

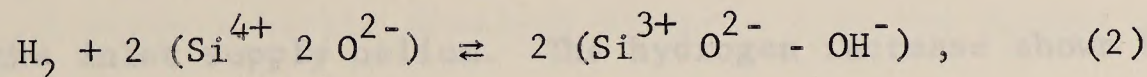
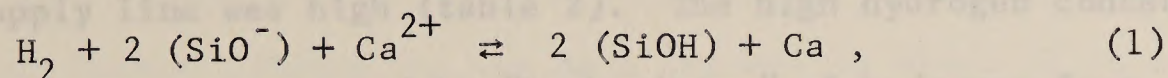
TABLE 2.-Results of freeze-out analyses on effluent helium from diffusion cell
using fourth set of quartz tubes

Cell oper time, hrs	Sample no	Type sample	Cell inlet press, psig	Cell oper temp, °C	Analysis, ppm							Total, less H ₂ O
					H ₂	Ne	O ₂	N ₂	Ar	CO ₂	CH ₄	
Supply helium (J225931) to cell					0	12.4	0.1	0.4	0	0	0	12.9
55	RT-1456	Composite	1,000	335	25.9	1.9	1.3	5.3	.1	<.05	0	34.5
148	RT-1457	Composite	1,000	335	4.2	2.7	.8	2.8	<.05	<.05	0	10.5
148	1/RT-1458	Direct	1,000	335	2.4	2.6	5.9	22.5	.3	<.05	0	33.7
172	1/RT-1460	Composite	700	335	6.7	4.9	27.2	105.9	1.3	.2	0	146.2
199	1/RT-1467	Composite	850	335	5.3	5.2	7.7	30.0	.4	<.05	0	48.6
223	RT-1471	Composite	850	402	4.4	5.2	1.0	4.1	<.05	<.05	0	14.7
319	RT-1481	Composite	500	454	5.4	13.2	1.2	4.8	.1	<.05	0	24.7
508	RT-1496	Composite	500	454	4.3	14.9	.2	.8	0	<.05	0	20.2
510	1/RT-1497	Direct	500	454	4.1	14.8	46.3	183.6	2.2	<.05	0	251.0
629	RT-1509	Composite	500	300	6.2	11.6	.4	1.4	0	0	0	19.6
699	1/RT-1523	Composite	500	550	17.2	21.4	49.5	194.0	2.3	.2	0	284.6
Residual helium in cylinder (675 psig)					0	14.3	.7	2.7	<.05	<.05	0	17.7
Inlet at series end (100 psig)					2/15.2	2/245.7	2/.5	2/556.9	2/1.5	2/138.4	2/14.3	2/972.5
New supply helium (H1141403) to cell					0	14.4	.6	2.4	0	.1	0	17.5
729	RT-1566	Composite	1,500	559	2.8	3.3	.4	1.7	0	.1	0	8.3
889	RT-1584	Composite	1,000	559	2.7	14.2	.5	1.7	0	0	0	19.1
1299	RT-1607	Composite	300	559	2.8	18.5	25.3	91.7	1.2	.2	0	139.7
Residual helium in cylinder (375 psig)					0	14.3	1.4	5.6	.1	.1	0	21.5
Inlet at series end (100 psig)					2/17.3	2/1845.7	2/0	2/97.2	2/.7	2/26.7	2/11.7	2/1999.3

1/ External air contaminated.

2/ Analysis by high pressure method (6).

R. W. Lee (3) postulated two side reactions during the manufacture of quartz:



both of which, he claims, could create relatively unstable hydroxyl ions in the quartz structure. The influence of heat and stress due to the quartz structure, or to unstable hydroxyl breakdown, Water as a possible source of the hydrogen is discounted because the oxygen in the residual helium in the inlet supply line was high (table 2) and the water content of the inlet gas was only about one ppm. Furthermore, the water content in the supply helium increases as the pressure drops, while the hydrogen content showed a decreasing trend. Hydroxyl breakdown was also eliminated as a source of the hydrogen because methane was not present in significant quantity in the inlet helium. This seems to be the basis for predicting equation (1) because the calcium impurity is greater in the natural variety.

When the third set of tubes was used, the analytical results (table 1) indicated that the hydrogen evolution was relatively low during the early use of the tubes. As shown in table 2, the reverse of this phenomenon occurred with the fourth set of tubes. Such a reversal cannot be associated with either pressure or temperature changes; the history of the tubes may have been different prior to their receipt at the Helium Research Center, or the tube sets may have been made of different types of quartz. The hydrogen evolution with the fourth set of tubes decreased rapidly during the first 100 hours of cell operation and remained at an essentially constant level for the remainder of the tests, except for analysis number RT-1523 (table 2) when the temperature was increased considerably. This hydrogen

increase was probably due, in part, to true diffusion because the quartz pores enlarged with increased temperature, and the hydrogen concentration in the helium supply line was high (table 2). The high hydrogen content in the inlet supply line was caused by "back-mixing" of hydrogen from the quartz with the inlet supply helium. The hydrogen increase shown by sample number RT-1523 could also have been due simply to the combination of increased pore size and increased activity of occluded hydrogen in the quartz structure, or to unstable hydroxyl breakdown. Water as a possible source of the hydrogen is discounted because the oxygen in the residual helium in the inlet supply line was low (table 2) and the water content of the inlet gas was only about one ppm. Furthermore, the water content in the supply helium increases as the pressure drops, while the hydrogen content showed a decreasing trend. Hydrocarbon breakdown was also eliminated as a source of the hydrogen because methane was not present in significant quantity in the inlet helium.

NEON DIFFUSION

The manufacturer of the purifier apparently assumed that none of the impurities in helium (except hydrogen to a limited extent above 450° C) would pass the quartz barrier, regardless of concentration in the inlet line. There is no provision in the cell for a continuous or intermittent purge of accumulated impurities from the inlet line. Tables 1 and 2 show that the manufacturer's assumption is not warranted when neon is present in the inlet helium. Neon diffusion through the quartz tubes increased with time due to an increase in concentration in

the supply helium (table 2). The most significant result discovered in this evaluation is the fact that neon passed through the quartz with apparent ease. Neon is the major impurity in Grade-A helium and is the most difficult to remove. Normally, the neon content is about 12 to 18 ppm in cylinders of Grade-A helium obtained directly from the Bureau of Mines.

Because neon passes through the quartz, it should be possible to determine permeability ratios for helium-neon mixtures from experimental data; this information would permit a reasonably good prediction of the neon content in the effluent helium from a quartz purifier. Diffusion and permeability constants vary (4, 5), depending on temperature and pressure, and their determinations were beyond the objective in this study. McAfee (4, 5) discusses the theory of glass diffusion in detail and gives various data on helium. Diffusion and permeability constants for both hydrogen and neon would be applicable when these gases were present in the supply helium.

CONCLUSIONS

The analysis of the effluent helium from the purifier shows that the utility of the purifier is limited because of anomalous hydrogen evolution plus the significant diffusion of neon through the quartz tubes.

The hydrogen evolution decreases eventually to acceptable limits for some uses of the purified helium from the cell; however, it may be necessary to expose the cell continuously to a helium shield if equa-

tions (1) and (2) are applicable. Estimation of the volume of helium necessary to pass through the cell to achieve complete removal of hydrogen is difficult because its concentration in the purified helium approaches zero almost asymptotically.

When a new neon-containing Grade-A helium cylinder is connected to the cell the following occurs: (1) the neon content in the effluent helium from the cell is at first about one-sixth of that in the supply helium; and (2) the cell acts as a dilution flask in reverse until the concentration of neon in the effluent helium is the same as that in the supply cylinder. If no purge has been made, this concentration limit in the inlet line will occur when about 40 percent of the supply helium has been used.

Except for hydrogen and neon, the quartz is almost, if not completely, nonpermeable to the impurities normally found in helium. A periodic blowdown, or a continuous fractional bleed, of the supply helium in the inlet line assists in decreasing all impurities in the purified helium. A cascade of cells would be beneficial when used in conjunction with other purification equipment.

Use of the cell by itself for purification of helium for such uses as chromatograph carrier gas does not produce helium containing less than one ppm total impurity. For the ultrapurification of helium, the purifier is less effective than a liquid-nitrogen-cooled charcoal trap.

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