164
8.10.76

81-261

MLM-2309

MLM-2309

**Transpiration of Helium and
Carbon Monoxide through a
Multihundred Watt, PICS Filter**

Dale R. Schaeffer

July 30, 1976

Monsanto

MOUND LABORATORY

Miamisburg, Ohio
operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

**UNITED STATES ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION**

U. S. Government Contract No. E-33-1-GEN-53

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Transpiration of Helium and Carbon Monoxide through a Multihundred Watt, PICS Filter

Dale R. Schaeffer

Issued: July 30, 1976

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price. Printed Copy \$3.50, Microfiche \$2.25

MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio 45342
operated for

UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

U. S. Government Contract No. E-33-1-GEN-53

INTRODUCTION

The generation of carbon monoxide within the Multihundred Watt (MHW) Isotopic Heat Source (IHS) has been established by numerous gas taps conducted at Mound Laboratory. Mass spectrometer analysis of the gas tap specimens invariably show a lower-than-normal $^{18}\text{O}/^{16}\text{O}$ ratio when CO and CO_2 are present in concentrations of greater than 10 mole %. This reduction is in the same order as that for oxygen in the $^{238}\text{PuO}_2$ fuel which has been treated with $^{16}\text{O}_2$ to reduce the neutron emission caused by the α, n reaction with ^{17}O and ^{18}O in natural oxygen. Since the fuel is involved in the reaction, transpiration of the gas species through filters present in each Post Impact Containment Shell (PICS) must occur. The two proposed reactions for the CO generation are: (1) CO/ CO_2 generation in the graphite followed by oxygen exchange with the fuel, and (2) a cyclic process involving reduction of the fuel by CO forming CO_2 followed by reduction of the CO_2 by graphite forming 2CO which again reduces the fuel, etc. This study was made to determine if the transpiration through the filters is fast enough to support either or both of the above reactions.

EXPERIMENTAL

The test consisted of placing reservoirs of helium and carbon monoxide on opposite sides of a MHW filter as shown in Figure 1. The MHW filter was welded normally into one half of a primary impact containment shell (PICS). The glass reservoirs were joined to the funnels by glass and tygon tubing. Inlets for evacuation and backfill were provided on both sides of the filter.

The reservoir on the fuel side of the filter was filled with 760 mm Hg of helium and the remaining reservoir was filled with 760 mm Hg of carbon monoxide. After the sealed reservoirs were installed in the test setup, the connections between the reservoirs were evacuated and backfilled with helium four times. The last helium backfill was to a pressure of 760 mm Hg. After the test system was isolated from the helium/vacuum supply, the test was started by opening the reservoirs. After a known period of time, the reservoirs were closed and the resultant gas mixtures were analyzed by mass spectrometry.

FIGURE 1 - Test setup for determining the He/CO transpiration rate through a MHW filter.

Separate tests were conducted to determine: (1) the pressure differential across the filter created by the difference in velocity between the helium atoms and carbon monoxide molecules, and (2) the pressure drop caused by the diffusion of helium through the plastic sections of the system. During the first test, the pressure on the CO side of the filter was continually monitored; and after the second test, the pressure in both reservoirs was measured after 140 hr. From these tests, it was concluded that the pressure differential was smaller than the sensitivity of the gage (≈ 0.5 mm Hg) and was therefore considered insignificant; and that the loss of helium was $\leq 1\%$ for the longest test period (285 hr) and thus, was also considered to be negligible.

Calculation of the initial amounts of helium and carbon monoxide on each side of the filter were made since the fill pressures and the volumes of the reservoirs and connections were known. Calculation of the final amounts of helium and carbon monoxide were made by taking the product of the mole fraction as determined by mass spectrometry and the total number of moles present at the start of the test. This calculation was valid since the final pressures in the reservoirs were determined to be equal to each other and the pressure at the start of the test.

RESULTS

A summary of the data is listed in Table 1 and is displayed in Figure 2 as a graph of the percent of the equilibrium amount which transpired versus time (assuming the concentration of CO on both sides of the filter is equal at equilibrium). The data was treated in two ways: first, by applying it to Fick's first law and second, by applying a rate equation for a first order, reversible reaction.

The data was applied to Fick's first law by relating the transpiration to diffusivity. Fick's first law states that the flux of a diffusing species is equal to the product of the concentration gradient and a diffusion coefficient or:

$$J = -D \left(\frac{dC}{dx} \right).$$

To determine the diffusion coefficient, the following assumptions were made:

1. The concentration gradient $\left(\frac{dC}{dx} \right)$ was taken to be the difference in concentration between the reservoirs divided by the average path length through the filter.

2. The flux (J) is defined as the number of moles coming through the surface area of the "void" portion of the filter, A, per second. It was found by determining the slope of the moles transferred versus the time curve.

The determinations for D were fairly constant and approximated 7.8×10^{-4} (cm $\cdot$ L)/sec where L is the average path length through the filter. Since D is independent of the concentration gradient, it will still apply to the lower CO concentration in the isotopic heat source (IHS).

Considering the test to be a first order, reversible reaction, it can be related to the following equation:

$$\frac{dA}{dt} = -k_1 A + k_2 B,$$

where: A is the concentration of CO on the outside of the PICS where it originated.

B is the concentration of CO on the inside of the PICS (fuel side).

k_1 is the rate constant for the CO moving to the inside of the PICS.

k_2 is the rate constant for the CO moving to the outside of the PICS.

After substitution and integration the equation becomes:

$$\ln \left(\frac{AK-B}{A_0K-B_0} \right) = -(k_2+k_1)t,$$

where: A₀ is the initial concentration of CO on the outside of the PICS.

B₀ is the initial concentration of CO on the inside of the PICS and is zero in this test.

$K = \frac{k_1}{k_2}$; for this test k_1 was assumed to equal k_2 and therefore $K = 1$.

Therefore:

$$\ln \left(\frac{A-B}{A_0} \right) = -(k_2+k_1)t.$$

A graph of the $\ln \left(\frac{A-B}{A_0} \right)$ versus time shown in Figure 3 verifies that the behavior of the filter is described by a first order, reversible reaction. Values for k_1 and k_2 are listed in Table 1 and averaged 0.0058 hr $^{-1}$. The half-life for the reaction is equal to $\frac{\ln 2}{k}$ or 120 hr. This is the time required for 50% of the CO to pass through the filter. The rate constant and the half-life for a first order reaction are independent of initial concentrations, therefore, both should be indicative of transpiration in the IHS.

Table 1

CO/He TRANSPIRATION THROUGH A MHW FILTER AT ROOM TEMPERATURE

Duration of Test		Moles ^a Transpired	Equilibrium Amount Transpired (%)	Flux at ^b Duration, J ($\frac{\text{moles}}{\text{A} \cdot \text{sec}}$)	Final ^c Concentration Gradient Across Filter dC/dX ($\frac{\text{moles}}{\text{cm}^3}/L$)	Diffusivity, D ($\text{cm} \cdot L/\text{sec}$)	k^d (hr^{-1})
(hr)	(sec)						
21	7.56×10^4	0.00235	22.3	2.64×10^{-8}	3.10×10^{-5}	8.5×10^{-4}	0.0062
48	1.73×10^5	0.00445	42.4	1.74×10^{-8}	2.29×10^{-5}	7.6×10^{-4}	0.0059
120	4.32×10^5	0.00765	72.9	8.55×10^{-9}	1.07×10^{-5}	8.0×10^{-4}	0.0056
168.5	6.07×10^5	0.00875	83.3	5.02×10^{-9}	6.51×10^{-6}	7.7×10^{-4}	0.0056
285	1.026×10^6	0.00995	94.8	1.10×10^{-9}	1.55×10^{-6}	7.1×10^{-4}	0.0057

^a Since the pressure on both sides of the filter remained equal during the tests, the amount of helium and carbon monoxide that transpired was equal.

^b A is the surface area of the "void" portion of the filter.

^c L is the average path length through the filter.

^d The rate constant applies to both the forward and reverse reactions since they were assumed to be equal.

FIGURE 2 - Percent of the equilibrium amount (0.0105 moles) of helium and carbon monoxide transpired through the MHW filter graphed as a function of time.

FIGURE 3 - Graph of the $\ln\left(\frac{A-B}{A_0}\right)$ versus time where A_0 is the initial concentration of CO on the outside of the PICS filter; and A and B are the CO concentrations after time t on the outside and inside of the PICS filter, respectively. The straight line proves transpiration is described by a first order, reversible reaction.

An effort to relate the room temperature data to the real situation present in the heat source was made by determining the relationship between the number of times each CO molecule collides with a given area every second in the 295 K test and in the 997 K⁽¹⁾ IHS. The number of collisions, N , is given by the following equation:⁽²⁾

$$N = \frac{u}{4V},$$

where: u is the average velocity of the molecule, and

V is approximately the volume of the system;

however, $u = \left(\frac{3RT}{M} \right)^{\frac{1}{2}},$

where: T is the temperature,

M is the molecular weight of CO, and

R is the gas constant.

therefore:

$$N = \frac{\left(\frac{3RT}{M} \right)^{\frac{1}{2}}}{4V}.$$

If the temperature of the system is increased from 295 K to 997 K, the number of collisions will be related as follows:

$$\frac{N_{997 \text{ K}}}{N_{295 \text{ K}}} = \frac{\left[\frac{3R(997)}{M} \right]^{\frac{1}{2}}}{\left[\frac{3R(295)}{M} \right]^{\frac{1}{2}}} = \frac{(997)^{\frac{1}{2}}}{(295)^{\frac{1}{2}}} = 1.8,$$

(1) 997 K was determined by averaging the 833 K IHS surface temperature and the 1116 K fuel surface temperature.

(2) This relationship assumes that the ratio of CO molecules that make it through the filter to the number that attempt it is the same with changing temperature. This is not necessarily true since the size of the holes in the filter might increase with temperature, which would increase the transpiration rate with increasing temperature.

assuming the volume remains constant. Therefore, the rate of transpiration should increase by a factor of about 1.8 as the temperature is increased from 295 to 997 K⁽³⁾.

Other factors that need to be considered when comparing the test and the expected behavior in the IHS are the number of vents in the systems and the volumes in the systems that are occupied by gas. This was accomplished by combining Fick's first law with the equation for a first order reaction. As previously mentioned, Fick's first law described the transpiration by the equation:

$$J = -D \frac{dC}{dX},$$

where the flux, J , is defined as the number of moles passing through the surface area of the "void" portion of the filter, A , per unit time. The equation can thus be written:

$$\left(\frac{dn}{dt} \right) \left(\frac{1}{YA} \right) = -D \frac{dC}{dX},$$

where Y is the number of filters in the system. Since $n/V=C$, we get the following expression of Fick's law:

$$\frac{dC}{dt} = - \left(\frac{YAD}{V} \right) \left(\frac{dC}{dX} \right).$$

The transpiration was also successfully described by a first order reversible reaction, which means that both the forward and reverse reactions can be described by:

$$\frac{dC}{dt} = -kC.$$

Substituting this expression for $\frac{dC}{dt}$ into Fick's law, we get:

$$kC = \left(\frac{YAD}{V} \right) \left(\frac{dC}{dX} \right).$$

(3) In collision theory of reaction velocity, the rate is equal to the product of the probabilities of collision and the possession of sufficient activation energy. In the present case, the activation energy can be neglected; and thus, the term showing the dependence of the reaction rate on the logarithm of the temperature has been omitted.

Assuming A and D are the same in the IHS as in the test⁽⁴⁾, and for the same CO concentration, C, and concentration gradient⁽⁵⁾, the equation becomes:

$$k = \frac{Y}{V} (S) ,$$

where S is a constant that is of equal value in the test and IHS. Therefore, the rate constant in the IHS is related to the rate constant of the test by:

$$k_{\text{IHS}} = (k_{\text{TEST}}) \left(\frac{V_{\text{TEST}}}{V_{\text{IHS}}} \right) \left(\frac{Y_{\text{IHS}}}{Y_{\text{TEST}}} \right) .$$

For the transpiration rate into the PICS, V_{IHS} is the volume in the IHS occupied by gas (excluding the volume in the PICS); therefore:

$$k_{\text{IHS}} = (0.0058 \text{ hr}^{-1}) \left(\frac{497 \text{ cc}}{3450 \text{ cc}} \right) \left(\frac{48}{1} \right) = 0.04 \text{ hr}^{-1}$$

$$\text{or } t^{1/2} = 17.3 \text{ hr} .$$

For the transpiration rate out of the PICS, V_{IHS} is the volume in the PICS that is occupied by the gas phase; therefore,

$$k_{\text{IHS}} = (0.0058 \text{ hr}^{-1}) \left(\frac{517 \text{ cc}}{312 \text{ cc}} \right) \left(\frac{48}{1} \right) = 0.46 \text{ hr}^{-1}$$

$$\text{or } t^{1/2} = 1.5 \text{ hr} .$$

Note that the rate constants for the transpiration into and out of the PICS are not equal as was assumed in the test. The difference in the values of k was caused by the difference in volume occupied by the gas inside the PICS and outside the PICS. The half-lives indicate that the average molecule spends only about 9% of time inside of the PICS. Combining the effects of volume, number of filters, and temperature, results in first order rate constants of 0.074 hr^{-1} ($t_{1/2} = 9.4 \text{ hr}$) for the transpiration into the PICS and 0.84 hr^{-1} ($t_{1/2} = 0.8 \text{ hr}$) out of the PICS.

(4) A and D are assumed constant to find the dependence of k on the volume and number of filters. Actually, D will increase with temperature as previously discussed, and A (the surface area of the "void" portion of the filter) will probably also increase with temperature.

(5) It is obvious that the concentration and concentration gradient will be larger in the test than in the IHS. However, k and D are independent of concentration; thus, the concentrations can be made to equal each other without changing k or D.

A third factor that would affect the comparison of the data from the test with expected behavior in the IHS is a change in the behavior of the filter with increasing temperature. As previously noted, it is probable that the size of the pores in the filter will increase with increasing temperature, thus increasing the rate of transpiration.

CO generation by the cyclic process requires an initial concentration of CO, CO_2 , or oxygen for initiation. The gas tap data requiring the largest initial concentration of CO was a generation rate of 0.01 atm/day after 15 days. This generation rate requires an initial concentration of about 0.04% CO if the sum of the half-lives into and out of the PICS is 24 hr. Since 0.04% is not unreasonable and since the estimated total for the half-lives is roughly 10 hr, the cyclic mechanism appears possible if transpiration is the limiting step in the kinetics of the process.

CONCLUSIONS

The transpiration of CO through the MHW filter can be described by Fick's first law or as a first order, reversible reaction. From Fick's first law, a "diffusion" coefficient of $7.8 \times 10^{-4} \text{ cm} \cdot \text{L/sec}$ (L is the average path length through the filter) was determined. For the first order reversible reaction, a rate constant of 0.0058 hr^{-1} was obtained for both the forward and reverse reactions (they were assumed to be equal). This corresponds to a half-life of 120 hr.

It was also concluded that the rate constants and thus the transpiration rates, which were determined for the test, are smaller than those expected in the IHS. The effect of increasing the number of filters, changing the volumes, and increasing the temperature, changes the rate constant of the transpiration into the PICS to roughly 0.074 hr^{-1} ($t_{1/2} = 9.4 \text{ hr}$) and out of the PICS to 0.84 hr^{-1} ($t_{1/2} = 0.8 \text{ hr}$).

Of the two suggested mechanisms for the generation of CO inside the IHS, the cyclic process requires a much larger rate of transpiration than the process requiring oxygen exchange of CO given off by the graphite. The data indicate that the cyclic process can provide the CO generation rates observed in the IHS gas taps if there is no delay in time for any other kinetic process involved in the formation of CO or CO_2 . Since the cyclic process (which requires the fastest rate of transpiration) appears possible, this study does not indicate which reaction is occurring but concludes both are possible.

DISTRIBUTION

EXTERNAL

TID-4500, UC-23 (156)

Consultants

C. F. Curtiss
University of Wisconsin
C. F. Eck
Miamisburg, Ohio
D. F. Griffing
Miami University
J. H. Leonard
University of Kentucky
R. E. Miers
Ft. Wayne, Indiana
W. E. Moddeman
University of Dayton Research Institute
G. W. Powell
Ohio State University
A. Shapiro
University of Cincinnati
H. F. Swift
University of Dayton Research Institute
D. White
University of Pennsylvania

J. A. Chacon, DAO
R. K. Flitcraft, MRC

INTERNAL

W. T. Cave
C. W. Huntington
R. R. Jaeger
E. W. Johnson
L. V. Jones
D. P. Kelly
D. R. Schaeffer (2)
L. B. Stevens
J. G. Villars (2)

Document Control
Library (15)
Publications