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MLM-1462

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D. L. Plymale

AEC Research and Development REPORT

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

MOUND LABORATORY

MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. GOVERNMENT CONTRACT NO. AT-33-1-GEN-53

Printed in the United States of America
Available from
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National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

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MLM-1462
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Date: January 2, 1968
Issued: May 1, 1968

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ABSTRACT

An exchange reaction between $^{238}PuO_2$ sol-gel microspheres and oxygen enriched in ^{16}O was performed at two temperatures, 700 and 850°C. A slower exchange rate was observed at 850°C and was thought to be due to the sintering of the microspheres. A neutron reduction, characteristic of an equilibrium condition, was observed at both temperatures; however, the spheres possessed a high neutron emission, probably due to light element impurities. An exchange reaction at 700°C coupled with sintering at 1200°C for several hours reduced the emission to the predicted value of 5.0×10^3 n/sec-g.

INTRODUCTION

The neutrons emitted from ^{238}Pu metal which contains no light element impurities are produced by spontaneous fission at the approximate rate of 2.5×10^3 n/sec-g.[1-3] The neutron emission rate from $^{238}PuO_2$ is much higher than the spontaneous fission value and is principally due to the (α,n) reaction with ^{17}O and ^{18}O. Normal $^{238}PuO_2$ contains 0.037% ^{17}O and 0.204% ^{18}O in the total oxygen and exhibits a neutron emission of approximately 19×10^3 n/sec-g. Therefore, an enrichment of $^{238}PuO_2$ with ^{16}O should result in a reduction in neutron generation. Such a reduction has been observed, and the preparation of $^{238}PuO_2$ powder enriched in ^{16}O by gaseous exchange has been reported.[4]

Plutonium-238 dioxide microspheres were prepared at this laboratory using the sol-gel technique.[5] An exchange reaction between these spheres and enriched oxygen was performed at two temperatures, 700 and 850°C.

EXPERIMENTAL

Plutonium-238 dioxide microspheres were prepared in this laboratory by the sol-gel process and allowed to air dry on filter paper for approximately 16 hr. Then the microspheres were heated in air, at a rate of 120°/hr, to 500°C to remove water and organics. These spheres contained a normal distribution of oxygen isotopes. The approximate isotopic composition of the plutonium is summarized in Table 1.

Samples of oxygen enriched in ^{16}O were prepared by this laboratory and were found, by mass spectroscopy, to contain only a trace of ^{17}O and 0.01% ^{18}O. A sample of oxygen enriched to 93% ^{18}O (0.4% ^{17}O) was obtained from Bio-Rad Laboratories.

Neutrons were counted with a precision long counter which uses a polyethylene moderated, boron trifluoride proportional counter. The kinetic data were obtained by neutron counting with a Series 9140, Texas Nuclear Corp. counter located outside the alpha glovebox in which the experiment was performed.

Table 1

ISOTOPIC COMPOSITION OF PLUTONIUM

Isotope	(wt %)
^{238}Pu	79
^{239}Pu	16
^{240}Pu	4
^{241}Pu	1
^{242}Pu	Trace

The $^{238}PuO_2$ spheres were weighed into small quartz containers, then heated in a quartz reaction chamber to the exchange temperature and outgassed under vacuum for 1 hr. Isotopically enriched oxygen was then allowed to pass into the evacuated chamber containing the sample. An experiment which coupled exchange at 700°C with sintering at 1200°C was unsuccessful; since a quartz reaction vessel was used, there may have been an exchange reaction between the quartz and the oxygen gas at 1200°C. Therefore, a system consisting of a McDanel AP-35 combustion tube and a Coors AD-99 combustion boat was employed at this higher temperature. In these experiments the exchange was carried out at 700 or at 850°C. Following the 700°C exchange reactions the system was heated to 1200°C under vacuum, and the microspheres were sintered for 4 hr.

RESULTS

Table 2 lists data obtained for the enriched ^{16}O exchange experiments. At 850°C the rate of exchange was slower than expected, and in 1 hr a reduction in specific neutron emission of only 9×10^3 n/sec-g was observed. Such a reduction did not indicate that equilibrium had been achieved during the hour. Theoretically, a reduction of approximately 14×10^3 n/sec-g should be obtained if equilibrium were reached. The value of 14×10^3 n/sec-g is the difference obtained in a previous experiment for normal oxide (19×10^3 n/sec-g) and the minimum obtained for PuO_2 powder enriched in ^{16}O (5×10^3 n/sec-g).[4] This slower exchange rate at 850°C was thought to be due to the sintering of the microspheres to a more dense species, thus reducing the diffusion rate of enriched oxygen into the sphere.

Equilibrium was reached when the exchange reaction was allowed to continue an additional 4 hr at 850°C. The total reduction in neutron emission was 15×10^3 n/sec-g.

Table 2

ENRICHED OXYGEN-16 EXCHANGE DATA

Exchange Temperature (°C)	Initial Neutron Emission[a] (n/sec-g)	Neutron Emission (n/sec-g) After Exchange Time of		Decrease in Neutron Emission (n/sec-g) After Exchange Time of	
		1 Hr	5 Hr	1 Hr	5 Hr
850	29×10^3	20×10^3	14×10^3	9×10^3	15×10^3
700	50×10^3	35×10^3	---	15×10^3	---
700→1050[b]	36×10^3	22×10^3	---	14×10^3	---

[a] Emission from samples after being heated to exchange temperatures then outgassed for 1 hr.

[b] Exchange reaction occurred at 700°C; then sample was heated to 1050°C in the enriched oxygen atmosphere.

At 700°C the reaction goes to completion rapidly. Table 2 shows that in 1 hr a reduction of 15 x 10^3 n/sec-g was obtained. This reduction represents an equilibrium condition; however, the spheres themselves have a high neutron emission, probably due to light element impurities. Table 2 also lists data obtained from these same spheres reacted at 700°C, but heated additionally to 1050°C in the enriched oxygen atmosphere. A reduction in emission from spheres with both normal and enriched oxygen indicated that some light element impurities were lost. Here again, the difference between the exchanged and non-exchanged material of 14 x 10^3 n/sec-g indicated an equilibrium condition.

To verify the presence of light element impurities in these spheres fired at low temperature, a series of spheres were sintered in air at 1200°C for 4 hr; then the neutron emission was determined. Emission values of approximately 19 x 10^3 n/sec-g for these spheres indicated a low concentration of light element impurities after sintering. Plutonium-238 dioxide prepared with a normal distribution of oxygen isotopes but a low concentration of light element impurities also exhibited a neutron emission of approximately 19 x 10^3 n/sec-g. The values obtained for these spheres before and after sintering are listed in Table 3.

Table 3

NEUTRON EMISSION DATA FOR $^{238}PuO_2$ MICROSPHERES CALCINED AT 1200°C FOR 4 HR

Sample	Weight of ^{238}Pu g	Neutron Emission Before Sintering (n/sec-g)	Emission After Sintering at 1200°C, (n/sec-g)
1	0.847	--	18 x 10^3
2	0.573	39 x 10^3 (850°C)	19 x 10^3
3	0.800	--	18 x 10^3
4	1.750	50 x 10^3 (700°C) 36 x 10^3 (1050°C)	19 x 10^3
5	0.202	55 x 10^3 (700°C)	22 x 10^3
			Avg = 19 x 10^3

To show how rapidly equilibrium was achieved, kinetic data were obtained by neutron counting outside the glovebox during an ^{18}O exchange experiment. Figure 1 is a plot of neutron emission vs time at 700°C for an exchange reaction with enriched ^{18}O. The reaction proceeded to equilibrium in 12-15 min. The reaction was first-order with respect to the concentration of ^{18}O as indicated previously.[4] A final neutron emission of 3.1 x 10^6 n/sec-g was obtained for this sample enriched in ^{18}O and constituted an enrichment from 0.204% to approximately 50% ^{18}O.

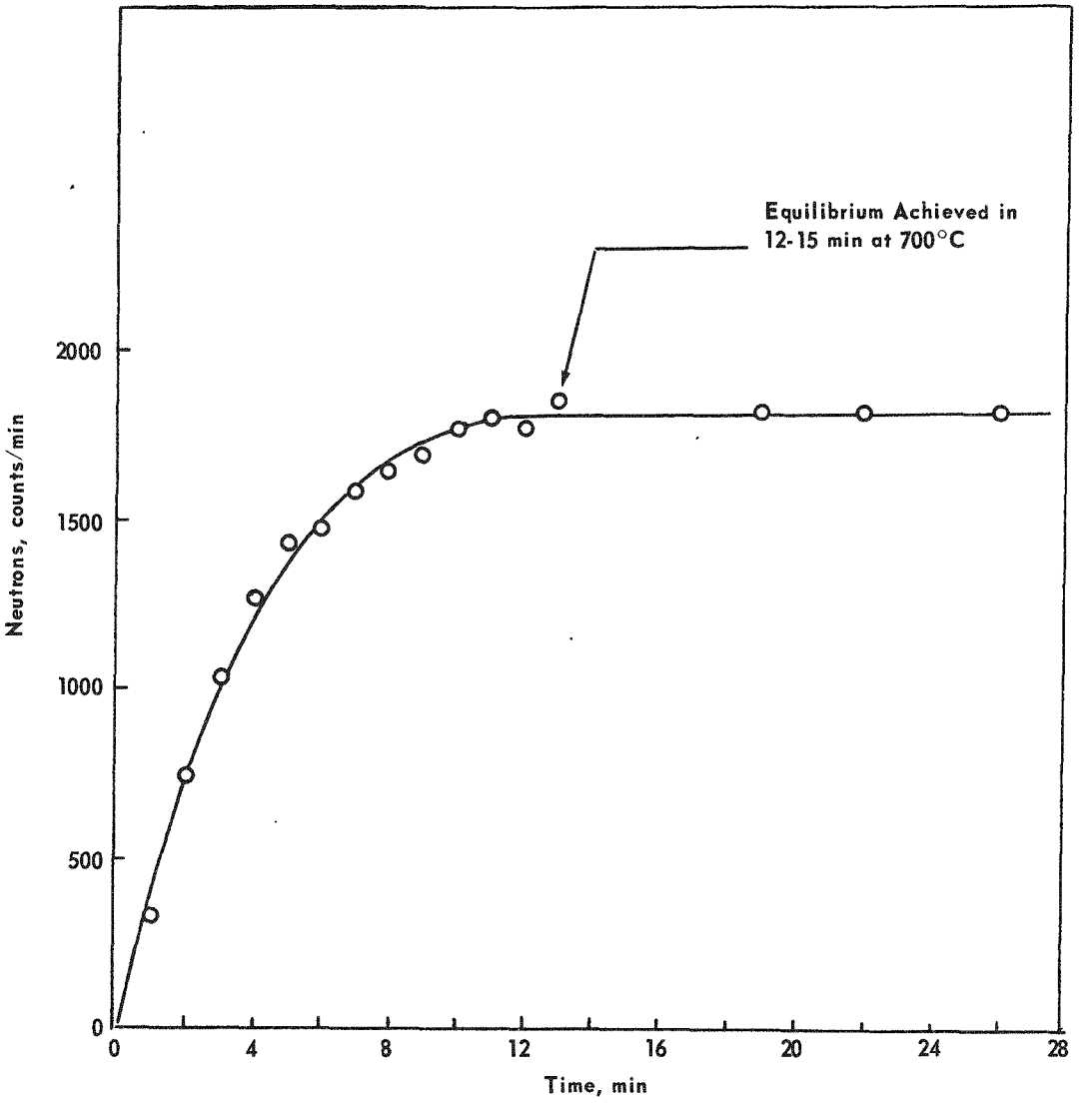

FIGURE 1 - The exchange of isotopically enriched ^{18}O with $^{238}PuO_2$ sol-gel microspheres at 700°C.

An exchange reaction at 700°C coupled with sintering at 1200°C for several hours should consistently produce $^{238}PuO_2$ with a neutron emission of approximately 5 x 10^8 n/sec-g. Such an experiment has also been performed with aluminum oxide system. The final neutron emission of 5.0 x 10^3 n/sec-g indicated the validity of this hypothesis.

ACKNOWLEDGMENT

The author wishes to thank M. E. Anderson and R. A. Neff of this Laboratory for their assistance in obtaining neutron emission data and R. L. Deaton of this Laboratory for experimental assistance.

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