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MOUND LABORATORY
Miamisburg, Ohio
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ABSTRACT

The results presented in this paper show that powder, particles, and pellets of $^{238}PuO_2$ undergo oxygen isotope exchange to form $^{238}Pu^{16}O_2$. Solid-solution ThO_2-PuO_2 also undergoes oxygen exchange to yield a fuel form with a low neutron flux. The experimental conditions which give best exchange results involve exchange and sintering at or above 1400°C. The rate data show that to completely exchange particles of PuO_2 in a period of time less than 1 hr temperatures in excess of 1300°C will be required. Pellets which have been sintered near 1600°C for several hours also exchange very slowly due to the presence of a diffusion-controlled reaction. The oxygen exchange of $^{238}PuO_2$ using a flowing gas system is also described.

INTRODUCTION

Plutonium-238 dioxide is a useful fuel for radioactive heat sources, being used in space missions, cardiac pacemakers, to power artificial heart pumps, and many other applications. Metallic plutonium-238 emits radiation which is mainly alpha particles and low energy gamma rays with only a small neutron flux of 2.5×10^3 n/sec-g ^{238}Pu due to the spontaneous fission of plutonium-238. Plutonium-238 dioxide has a neutron flux which is considerably higher, being about 19×10^3 n/sec-g ^{238}Pu. The increase in the neutron flux of plutonium-238 dioxide is due to the (α,n) reaction with oxygen-17 and oxygen-18. Plutonium dioxide which contains a normal oxygen distribution contains 0.037% oxygen-17 and 0.204% oxygen-18. Therefore, an enrichment of oxygen-16 in plutonium-238 dioxide should result in a decrease of the neutron flux as compared to normal plutonium-238 dioxide and this fact has been demonstrated.[1-5] In many of the heat source applications a low neutron flux is highly desirable or even a requirement.

The preparation of $^{238}Pu^{16}O_2$ has been demonstrated in two ways. Plymale used oxygen gas enriched in oxygen-16[2,3] while Porter and Thompson used $H_2{}^{16}O$.[4,5] Plymale's work involved the exchange of plutonium dioxide prepared by the thermal decomposition of plutonium(III) oxalate[2] and the exchange of sol-gel microspheres.[3] Using oxygen-18, he showed that over the temperature range of 850-1050°C the exchange reaction between oxygen-18 and oxalate-prepared plutonium dioxide reached equilibrium in 15-20 min. The reaction was first order with respect to $[^{18}O_g]$; however, no rate constants were reported. For exchange with oxygen-16 a discrepancy was found between the theoretical neutron flux and the experimental emission rate which was attributed to the presence of impurities in the plutonium dioxide which also undergo an (α,n) reaction.

The exchange of plutonium dioxide sol-gel microspheres appears to be more complex. At 700°C equilibrium was attained in 12-15 min; however, at 850°C 5 hr were required before equilibrium was attained. The difference in exchange rates was attributed to the sintering of the microspheres to a more dense species, thus reducing the diffusion rate of the enriched oxygen into the sphere. Sintering the exchanged microspheres at 1200°C caused a further reduction in the neutron count over that of material exchanged at 700°C, presumably because of the volatilization of light element impurities. The lowest neutron fluxes were obtained on samples exchanged at 700°C and then sintered at 1200°C.

Porter and Thompson studied the exchange of plutonium dioxide with $H_2{}^{16}O$.[4,5] They found that exchange was measurable at temperatures as low as 100°C (20% of equilibrium was reached in 2 hr), and that at 700°C equilibrium was attained within 30 min. At equilibrium,however, the oxygen-18 content did not agree with that predicted by material balance calculations. Plutonium-239 dioxide microspheres which had been dried at 120°C gave the same "exchange rates" as plutonium-239 dioxide powder and plutonium-238 dioxide powder.[5] However, microspheres which were sintered at 1100°C were almost completely inert toward oxygen exchange. The preparative method for obtaining these microspheres was not mentioned but they were about 100 μm in diameter. The rate of exchange was not found to be dependent upon the water pressure. Column exchange tests were also evaluated.

Since the above results raise many questions it was decided to continue the oxygen exchange study toward obtaining answers for some important questions. Particularly, is dense, high-fired plutonium dioxide really unreactive toward the oxygen exchange reaction and will such a treatment "fix" it and prevent a reexchange reaction? What is the cause of the difference in exchange rates between microspheres and plutonium dioxide powder? Finally, the consideration of using a ThO_2-PuO_2 solid-solution fuel in the radioactive heat sources aroused interest in the oxygen exchange of this material. The data and results in this paper will be divided into three parts and will be followed by a general discussion of their combined significance. The first part will deal with batch studies made with various materials. Secondly, rate data will be discussed, and the third part will deal with the study involving a flowing gas system.

PART I

Part I is concerned with the ability to reduce the neutron flux of ${}^{238}PuO_2$ by preparing ${}^{238}Pu{}^{16}O_2$; that is, under what conditions will the oxygen exchange reaction proceed. Depending upon the conditions of the exchange reaction either of two exchange apparatus was used. Both were similar differing mainly in size and temperature capability. They consisted of a high purity alumina reaction tube (McDanel AP-35 or equivalent) closed at one end, which could be heated in a platinum resistance furnace. The open end of the tube was fitted with either a quartz standard taper sufficiently far removed from the furnace to prevent overheating or by a water-cooled Veeco fitting. Both systems were constructed with sufficient outlets to allow a vacuum to be obtained, the pressure to be measured, and the oxygen-16 gas to be admitted to the system. The entire system is similar to that shown in Figure 1 used to obtain the rate data in Part II. The samples were placed in high purity alumina boats for the exchange studies. Since the exchange parameters varied from run to run they will be discussed with the experimental results.

The results presented in this section are concerned mainly with the exchange of particles and powder of plutonium dioxide and of ThO_2-PuO_2 solid solution in various configurations. Plutonium dioxide powder was prepared by the thermal decomposition of plutonium oxalate. Material prepared in this manner has a particle diameter of less than 10 μm with an average particle size of several micrometers.[6] The particles of plutonium dioxide were prepared by a hydroxide precipitation technique.

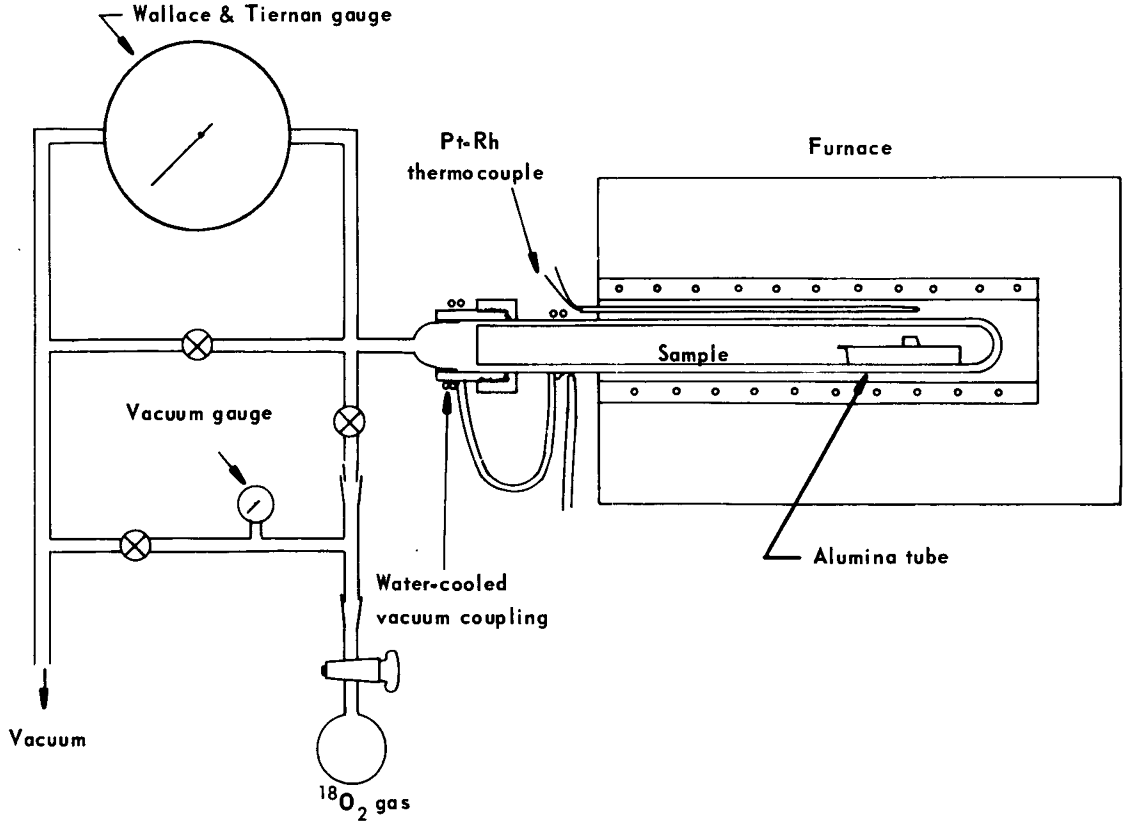

FIGURE 1 - Wallace & Tiernan Gauge.

A plutonium nitrate solution in nitric acid was added dropwise to an aqueous ammonia solution. The hydroxide was filtered, washed with dilute ammonium hydroxide and water, and allowed to self dry at temperatures below 100°C. The material was then sized, generally using the size range 125-297 μm.

Solid-solution particles of ThO_2-PuO_2 were prepared by precipitating with ammonium hydroxide a homogeneous solution of plutonium nitrate and thorium nitrate. The particles were treated in the same manner as particles of pure plutonium dioxide. Both the plutonium dioxide and the solid solution yielded particles of 95% theoretical density after calcining at 1000°C. Although solid solution of any weight percent thoria could be prepared by this technique, the exchange studies were all conducted on 10 ± 1 wt % ThO_2-PuO_2. Solid solution was confirmed by measuring the x-ray lattice parameters and by observing the photomicrographs of the particles. Microprobe results on these particles showed them to be homogeneous throughout in both plutonium and thorium. The impurity analysis of the solid-solution material is typical of that obtained for hydroxide-precipitated plutonium dioxide and similar to that reported by Plymale.[2]

Exchange studies were also carried out on pressed pellets of mixed powders of PuO_2 and ThO_2. Both powders were obtained by the thermal decomposition of the metal oxalate. The powders were thoroughly mixed by grinding in a mortar and pestle. Pellets, ¼ in. in diameter, were then pressed using a force between 25,000 and 60,000 psi. The raw pellets had a density of about 40% theoretical, while the sintered pellets were between 75 and 90% theoretical.

The oxygen-16 gas used in this study was prepared at this laboratory. The isotopic purities of the gas samples used are shown in Table 1.

Table 1

ISOTOPIC PURITIES OF GAS SAMPLES

Gas Sample	Oxygen Isotope (%)		
	Oxygen-16	Oxygen-17	Oxygen-18
1	99.99	0.0067	0.0047
2	99.99	0.0054	0.0063
3	99.99	0.0062	0.0057
4	99.99	0.0059	0.0053

The initial purpose of these experiments was to determine at what temperature which particles would undergo exchange. Table 2 lists the pertinent data. The procedure used to obtain these data is as follows: The samples were loaded into the appropriate reaction tube and, with the sample under air, the furnace was heated to the exchange temperature. Upon reaching the exchange temperature the system was evacuated and then backfilled with oxygen-16 to the desired pressure. After the oxide and gas equilibrated for 10 min, the system was again evacuated and then backfilled with oxygen-16. This process was repeated anywhere from 8 to 14 times. The exchanged oxide was allowed to cool under an oxygen-16 atmosphere. The sample was then neutron counted with a precision long counter which uses a polyethylene-moderated boron-trifluoride proportional counter to determine the degree of exchange.

Table 2

NEUTRON EMISSION RATES OF DIFFERENT FORMS OF PuO_2 BEFORE AND AFTER OXYGEN EXCHANGE

Sample	Neutron Emission (n/sec-g ^{238}Pu)	Exchange Temp. (°C)	Sinter Temp. (°C)	Notes
H-4	32×10^3	---	---	Hydroxide PuO_2 as received
H-5	16.7×10^3	---	1400	Hydroxide PuO_2 sintered and outgassed
O-2	18×10^3	---	---	Oxalate PuO_2 as received
O-3	21×10^3	---	1400	Oxalate PuO_2 sintered and outgassed
SS-3-0	70×10^3	---	---	ThO_2-PuO_2 solid solution as received
SS-3-OS	20×10^3	---	1400	ThO_2-PuO_2 solid solution sintered and outgassed
P-1-01	16.9×10^3	1600	---	ThO_2-PuO_2 pressed pellet, re-exchange study, held at 1600°C for 1 hr.
H-1	7.5×10^3	700	1400	Hydroxide PuO_2, 2 g of material, exchanged with H-2 and SS-1
H-2	6.7×10^3	700	1400	Hydroxide PuO_2, 8 g of material, exchanged with H-1 and SS-1
H-3	6.5×10^3	700	1400	Hydroxide PuO_2, 2 g of material, exchanged with SS-2 and O-1
SS-1	9.5×10^3	700	1400	ThO_2-PuO_2 solid solution, exchanged with H-1 and H-2
SS-2	7.3×10^3	700	1400	ThO_2-PuO_2 solid solution, exchanged with H-3 and O-1
O-1	5.9×10^3	700	1400	Oxalate PuO_2, exchanged with H-3 and SS-2
H-7	11.6×10^3	700	700	Hydroxide PuO_2, outgassed 1 hr at 740°C under vacuum, exchanged with H-8
H-8	15.8×10^3	700	700	Hydroxide PuO_2, not outgassed, exchanged with H-7
P-1-2	7.9×10^3	1600	1600	ThO_2-PuO_2 pressed pellet, originally P-1-01
P-2-2	11.2×10^3	1600	1600	ThO_2-PuO_2 pressed pellet, sintered 6 hr at 1600°C prior to exchange
P-2-2-2	14.5×10^3	1600	1600	Pellet P-2-2 re-exchanged in air
P-2-2-2-2	11.8×10^3	1600	1600	Exchanged with Pellet P-2-5, sintered at 1600°C about 10 hr
P-2-5	4.2×10^3	1600	1600	Exchanged with P-2-2-2-2, not sintered prior to exchange
P-2-3	4.9×10^3	1400	1400	ThO_2-PuO_2 pressed pellet, exchanged with H-9

Table 2 (continued)

Sample	Neutron Emission (n/sec-g ^{238}Pu)	Exchange Temp. (°C)	Sinter Temp. (°C)	Notes
P-2-4	3.9×10^3	1400	1400	ThO_2-PuO_2 pressed pellet, exchanged with H-10, SS-4-1, and SS-4-2
H-9	4.4×10^3	1400	1400	Hydroxide PuO_2, exchanged with P-2-3
H-10	4.5×10^3	1400	1400	Hydroxide PuO_2, exchanged with P-2-4, SS-4-1, SS-4-2
SS-4-1	4.3×10^3	1400	1400	Solid solution particles <105 μm, exchanged with P-2-4, H-10, and SS-4-2
SS-4-2	3.9×10^3	1400	1400	Solid solution particles 105-177 μm, exchanged with P-2-4, H-10, and SS-4-1
P-3-1	4.6×10^3	700	1400	ThO_2-PuO_2 pressed pellet, ½ in. diameter pellet
P-6-T_3	4.9×10^3	1400	1400	ThO_2-PuO_2 pressed pellets, top 3 pellets exchanged with P-6-M_4, P-6-B_4
P-6-M_4	4.8×10^3	1400	1400	ThO_2-PuO_2 pressed pellets, middle 4 pellets exchanged with P-6-T_3, P-6-B_4
P-6-B_4	4.7×10^3	1400	1400	ThO_2-PuO_2 pressed pellets, bottom 4 pellets, exchanged with P-6-T_3 and P-6-M_4
13-7	10.2×10^3	700	---	Hydroxide PuO_2 sintered 1 hr at 1300°C prior to exchange
16-7	17.2×10^3	700	---	Hydroxide PuO_2 sintered 1 hr at 1600°C prior to exchange
16-13	17.4×10^3	1300	---	Hydroxide PuO_2 sintered 1 hr at 1600°C prior to exchange
H-6	4.1×10^3	700	1400	Hydroxide PuO_2
H-6-1	4.5×10^3	700	1400	Hydroxide PuO_2, open to air at room temperature for 1 week
H-7-1	16.0×10^3	700	700	Hydroxide PuO_2, open to air at room temperature for 1 week
H-6-2	4.7×10^3	700	1400	Hydroxide PuO_2, open to air at room temperature for 1 month
H-1-1	21.9×10^3	700	1400	Hydroxide PuO_2, held at 200°C for 1 month in air atmosphere
13	18.5×10^3	---	1300	Hydroxide PuO_2
10	22.6×10^3	---	1000	Hydroxide PuO_2

It should be noted that the final neutron counts as listed in Table 2 give only qualitative results since different exchange procedures were used in many cases. Often, however, several samples were exchanged at the same time and these results are directly comparable. In addition, much qualitative information is available from these results.

The first six samples in Table 2 show the effect of sintering and outgassing on the neutron count. The sintering was done at 1400°C for 1½ hr. The outgassing was completed by occasionally evacuating the system to less than 1 mm Hg and then refilling with air.

Comparison of samples H-7 and H-8 shows the effect of only outgassing at 700°C. Sample H-7 was held under vacuum for 1 hr at 700°C. H-7 and H-8 were then exchanged together at 700°C in the usual manner but they were not sintered above the exchange temperature. It can be seen that outgassing at 700°C does have some effect on the neutron count.

Although the initial neutron flux due to impurities varies from one preparation to the next, these results show that with a combination of sintering and outgassing the sample, the neutron flux can be reduced to between 16×10^3 and 21×10^3 n/sec-g ^{238}Pu. The results also indicate that outgassing alone does not remove all the light element impurities, but the neutron count of sample 13 suggests that sintering without outgassing may be sufficient in removing all the light element impurities that lead to a high neutron flux. P-1-01 is a pressed pellet of 10 wt% ThO_2-PuO_2 sintered in air whose neutron emission rate was reduced to 16.9×10^3 n/sec-g ^{238}Pu.

Samples H-1, H-2, H-3, SS-1, SS-2, and O-1 were run to verify the exchange of hydroxide-precipitated plutonium-238 dioxide, oxalate-precipitated plutonium dioxide, and hydroxide-precipitated solid solution. The exchange was done at 700°C in the usual manner. The sample was then sintered at 1400°C for 1 hr using one tube of oxygen-16. The ratio of sample size to reaction tube volume was such that if the sample did not exchange at 700°C there would not be sufficient oxygen present at 1400°C to significantly reduce the neutron counts. SS-1, H-1, and H-2 were exchanged together as was O-1, H-3, and SS-2. Comparison of H-1 and H-2 suggests that exchange occurs equally well regardless of the bulk of plutonium-238 dioxide concentrated in a given area since H-2 involved the exchange of 8 g whereas H-1 contained only 2 g.

It has been shown that plutonium-238 dioxide, both hydroxide-precipitated and oxalate-precipitated, undergoes exchange at 700°C but that sintering above that temperature is required to obtain a low neutron count. On a production type process it would be helpful if exchange and sintering could be carried out simultaneously. P-2-3, a pellet of ThO_2 and PuO_2, and H-9 were sintered and exchanged simultaneously at 1400°C in the usual manner. Both samples underwent exchange. P-2-4, H-10, SS-4-1, and SS-4-2 were also sintered and exchanged together at 1400°C and good exchange was obtained. SS-4-1 was solid-solution particles less than 125 μm in diameter while SS-4-2 was particles 125-297 μm in diameter.

Comparison of these two samples shows that particle size is unimportant when comparing the exchange of similar material.

Since previously published results suggest that highly dense refractory oxide does not undergo oxygen exchange, a pellet of ThO_2-$^{238}Pu^{16}O_2$ was pressed and exchanged with normal oxygen. The $^{238}Pu^{16}O_2$ used to press the pellet was sample O-1 and the neutron count of the raw pellet should be about 5.9 x 10^3 n/sec-g ^{238}Pu. After this pellet, P-1-01, was sintered at 1450°C in air for 1 hr the neutron count increased to 16.9 x 10^3 n/sec-g ^{238}Pu indicating complete reexchange. The results for the exchange of P-1-2 indicate that pellets do undergo oxygen-16 exchange. To check the effect of sintering a pellet prior to exchange, P-2-2 was sintered for 6 hr at 1600°C prior to exchange. Since oxygen exchange of this pellet reduced the neutron count to only 11.2 x 10^3 n/sec-g ^{238}Pu, the densification of the pellet apparently retarded the exchange. After sintering in air for 6 hr, the neutron count of the same pellet, P-2-2-2, only reached 14.5 x 10^3 n/sec-g ^{238}Pu. After sintering an additional 2 hr for a total of 14 hr, P-2-2-2-2 was oxygen-16 exchanged to a final neutron count of 12 x 10^3 n/sec-g ^{238}Pu. To ensure that exchange was taking place pellet P-2-5 (not sintered) was exchanged with P-2-2-2-2 to a final neutron count of 4.2 x 10^3 n/sec-g ^{238}Pu. These results suggest that a large mass of dense refractory oxide is somewhat inert toward oxygen exchange and that sintering in fact reduces the rate of oxygen exchange.

Sample P-3-1 is a ½-in. pellet which was exchanged at 700°C and sintered at 1400°C. The final neutron count, 4.6 x 10^3 n/sec-g, shows that densifying large masses of plutonium dioxide by compaction does not hinder the exchange and that larger pellets exchange as well as do the smaller pellets.

Another check on the effect of bulk on exchange was made by placing the exchange tube in a vertical position and stacking eleven ¼-in. pellets on top of one another. These are labeled P-6-T_3, P-6-M_4, and P-6-B_4. Exchange results showed that the top three, the middle four, and the bottom four pellets all exchanged to the same extent.

All the exchange results thus far reported have been on samples which were not sintered above the exchange temperature prior to exchange. To determine whether material sintered at a temperature above the exchange temperature would undergo the oxygen exchange reaction samples 16-7, 16-13, and 13-7 were run. Hydroxide plutonium dioxide sintered at or above 1300°C underwent only limited exchange at 700°C. The same material sintered at 1600°C underwent a higher degree of exchange at 1300°C than at 700°C, however exchange was still not complete.

There remains the question of reexchange during normal handling of the plutonium oxide. H-6 is a hydroxide-precipitated sample which was exchanged at 700°C and then sintered at 1400°C while H-7, as discussed above, was only exchanged at 700°C. After exposure to the air at room temperature for one week the unsintered plutonium-238 dioxide (H-7-1), showed some reexchange while the material sintered at 1400°C (H-6-1), showed no reexchange. After exposure for an additional month H-6-2 still had the same neutron count as H-6. Sample H-1 was held at 200°C for one month in an air atmosphere, and H-1-1 shows that this sample underwent nearly complete reexchange. H-1 had been sintered at 1400°C. These results suggest that if a large quantity of plutonium-238 dioxide is to be stored it will have to be stored under oxygen-16 as the ambient temperature will be greater than 200°C.

The initial experiments in this part have shown that sintering and outgassing at 1400°C removes all the light element impurities which also undergo (α,n) reactions and give larger than anticipated neutron fluxes. Certainly the extent of oxygen-16 exchange is limited by the extent to which the oxygen-17 and oxygen-18 are depleted in the enriched oxygen sample; however, the best exchange obtained based upon the final neutron count is only about 93%. The complete exchange of this material based upon the purity of the gas used should be in excess of 98%. The neutron spectrum of sample SS-4-2 was obtained to determine whether any part of the final neutron flux could be attributed to impurities. The total increase in the neutron flux over the spontaneous fission of plutonium-238 could be attributed to the oxygen-18 present in the oxide. This suggests that each exchange did not come to 100% of the expected equilibrium value. This fact will be discussed later.

PART II

The second part of this paper is concerned with the rate of exchange of plutonium dioxide. In Part I it was shown that good exchange and low neutron fluxes can be obtained with hydroxide-precipitated and oxalate-precipitated pure plutonium oxide, with hydroxide-precipitated solid solution and with blended ThO_2-PuO_2 pellets. The question remains, what are the best conditions for exchange?

Plymale has shown that it is possible to obtain kinetic data for oxygen exchange of $^{238}PuO_2$ by following the increased neutron counts which occur during oxygen-18 exchange.[2,3] A similar procedure was used to obtain kinetic data for the oxygen exchange of hydroxide-precipitated and oxalate-precipitated plutonium-238 dioxide.

Oxygen-18 was prepared in this laboratory by electrolysis of $H_2{}^{18}O$ using sodium as the electrolyte. The apparatus used is shown in Figure 2. The receiver flask was a 1-liter round bottom fitted with a 10/30 standard taper joint. After one liter of gas was collected, it was condensed in the charcoal trap with the use of liquid nitrogen. The oxygen-18 was then transferred to 200-ml round bottom flasks for the exchange studies. The oxygen gas was analyzed by mass spectrometry and the results are shown in Table 3.

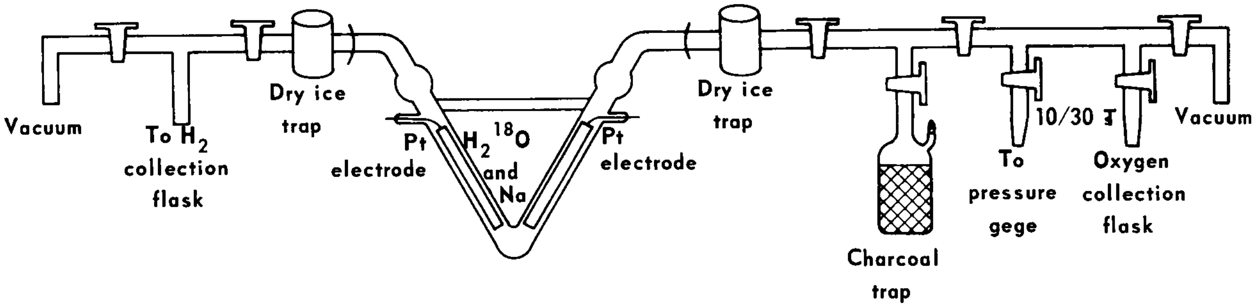

FIGURE 2 - Apparatus used to prepare oxygen-18.

Table 3

OXYGEN-18 GAS ANALYSIS

Sample	H_2[a] (%)	H_2O[a] (%)	CO[a] (%)	CO_2[a] (%)	O_2[a] (%)	$^{18}O_2$[b] (%)
1	0.22	0.13	0.85	0.77	94.66	97.24
2	0.037	0.08	0.74	0.91	95.97	97.01
3	0.012	0.08	0.52	0.57	98.08	97.97
4	0.008	0.10	0.48	0.58	98.39	97.48

[a] The percentages are given as mole percent. The system was purged with argon prior to electrolysis and the remaining gas impurity was argon.

[b] The oxygen-18 analysis is given as mole percent of total oxygen.

The exchange reaction was followed by monitoring the increase in neutron count through the hood front of an alpha box. A Texas Nuclear series 9148 neutron counter was used to follow the reaction. The reaction tube was similar to that used in the batch experiments described in Part I and shown in Figure 1. Approximately 0.15 g of plutonium-238 dioxide was weighed into a high purity thoria crucible. The volume of the system was 207 ml, and about 200 mm Hg of oxygen was used. The average gas temperature was calibrated prior to the exchange studies.

Several assumptions are required to obtain meaningful rate data from this system. Since about 97% of the volume of the system was in the main reaction tube the assumption that complete gas mixing has occurred is undoubtedly valid. It was also assumed that the system is inert toward oxygen exchange. Literature data suggest that this is true for high purity alumina up to 1600°C[7] and the present results suggest that it is also true for the rest of the system. Oxygen gas samples taken after equilibrium had been obtained and the final neutron count of the plutonium dioxide sample indicated that equilibrium had been obtained and that only the plutonium dioxide underwent exchange.

The oxygen isotope exchange reactions of plutonium-238 dioxide at 1000°C prepared by the oxalate and hydroxide methods are shown in Figure 3. The exchange of the oxalate material at 700, 1000, 1300, and 1550°C gave curves similar to that shown in Figure 3 with equilibrium being attained between 15 min at 700°C and 5 min at 1550°C. The hydroxide material took hours to attain equilibrium at 700, 1000, and 1300°C; however, at 1550°C equilibrium was reached in about 16 min as shown in Figure 4.

Plymale has shown that oxygen exchange with plutonium dioxide is first order with respect to $[^{18}O_g]$. For such a reaction a plot of log $\{[^{18}O_g]_t - [^{18}O_g]_\infty\}$ as a function of time should be linear. Figure 5, which shows such a plot, confirms that the exchange reaction is first order with respect to $[^{18}O_g]$. All the exchange reactions observed during this study were found to be first order. The rate constants, which are the slope of the line in Figure 5, are given in Table 4.

The results for the exchange of hydroxide-precipitated plutonium dioxide as shown in Figure 3 suggest that the exchange consists of two reactions, an initial fast reaction and a second slower reaction. The rate constants given in Table 4 are the initial rates for the exchange reaction. Similar curves have been reported in the literature.[8] The initial reaction has been attributed to a surface exchange while the slower reaction involves self-diffusion of oxygen to the particle interior.

The rate constants given in Table 4 are the measured rate constants. For the exchange of hydroxide-precipitated plutonium dioxide at temperatures of 1300°C and lower, the rate constant k is a sum of k_1 and k_2 where k_1 is the surface exchange rate constant and k_2 is the self-diffusion rate constant. Because of the complexity of the observed rate constants at these temperatures they were not calculated.

Table 4

EXCHANGE PARAMETERS AND RATE CONSTANTS FOR THE OXYGEN EXCHANGE OF PuO_2

Sample Preparation	Sintering Temperature	Exchange Temperature	Equilibration Time	$[^{18}O_g]_\infty$	Rate Constant
Oxalate	1550°C	1550°C	5 min	59.3%	85.8 x 10^{-2} min^{-1}
	1300	1300	6 min	71.7	66.3
	1000	1000	12 min	73.3	30.7
	700	700	15 min	71.8	27.7
	1550	1000		73.3	36.2
Hydroxide	1550	1550	16 min	70.5	22.5
	1300	1300	~1 hr	70.8	
	1550	1300	>1 hr	71.2	
	1000	1000	>1 hr	70.7	
	700	700	>2 hr	72.7	
[a]	1550	1550		72.0	26.4
[b]	1550	1550		70.9	35.5
[c]	1550	1550		72.6	25.1

[a] Sintered an additional 6 hr at 1550°C.

[b] Fines (10-125 μm) sintered 6 hr at 1550°C.

[c] New preparation of PuO_2.

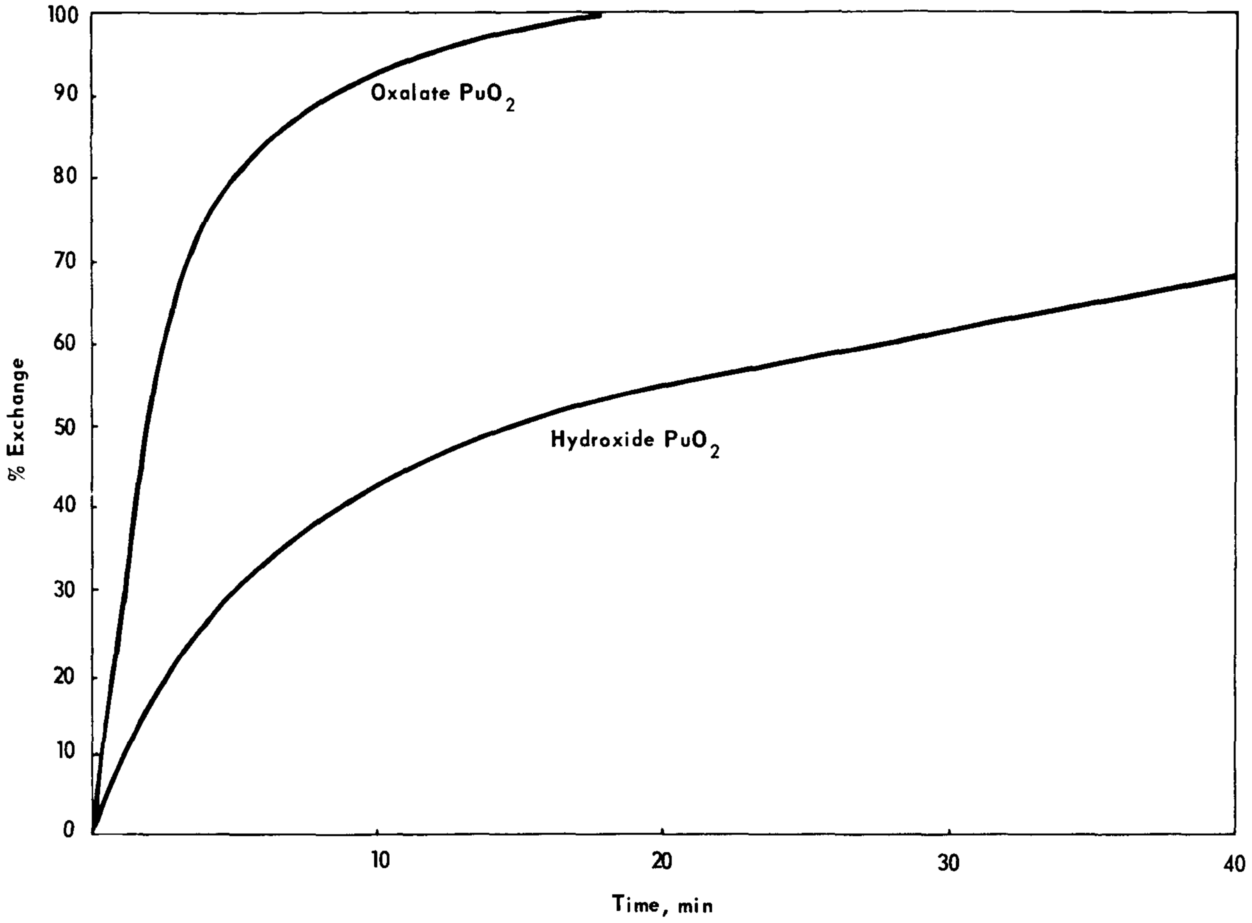

FIGURE 3 - Exchange reaction at 700°C of hydroxide and oxalate PuO_2.

The rate constants given in Table 4 and as seen in Figure 3 show quite dramatically that the method of preparation of plutonium dioxide has a considerable effect on the oxygen isotope exchange reaction, a fact which appears not to have been fully appreciated in previous reports. This fact is not surprising, however, considering the large differences in microstructures of plutonium dioxide prepared by various methods and the fact that larger particles of plutonium dioxide exchange by a diffusion process.

That the hydroxide-prepared plutonium dioxide exchanges by a diffusion process is substantiated by the results shown in Figure 6. Sintering of hydroxide plutonium dioxide at 1550°C lowers the rate of exchange at 1000°C, whereas sintering of oxalate plutonium dioxide has no effect on the exchange rate. Since nearly maximum density is reached by 1000°C the sintering effect only causes a grain growth, and therefore the slower diffusion exchange mechanism becomes more predominant. As shown in Table 4, a change in the particle size has only a small effect on the exchange rate.

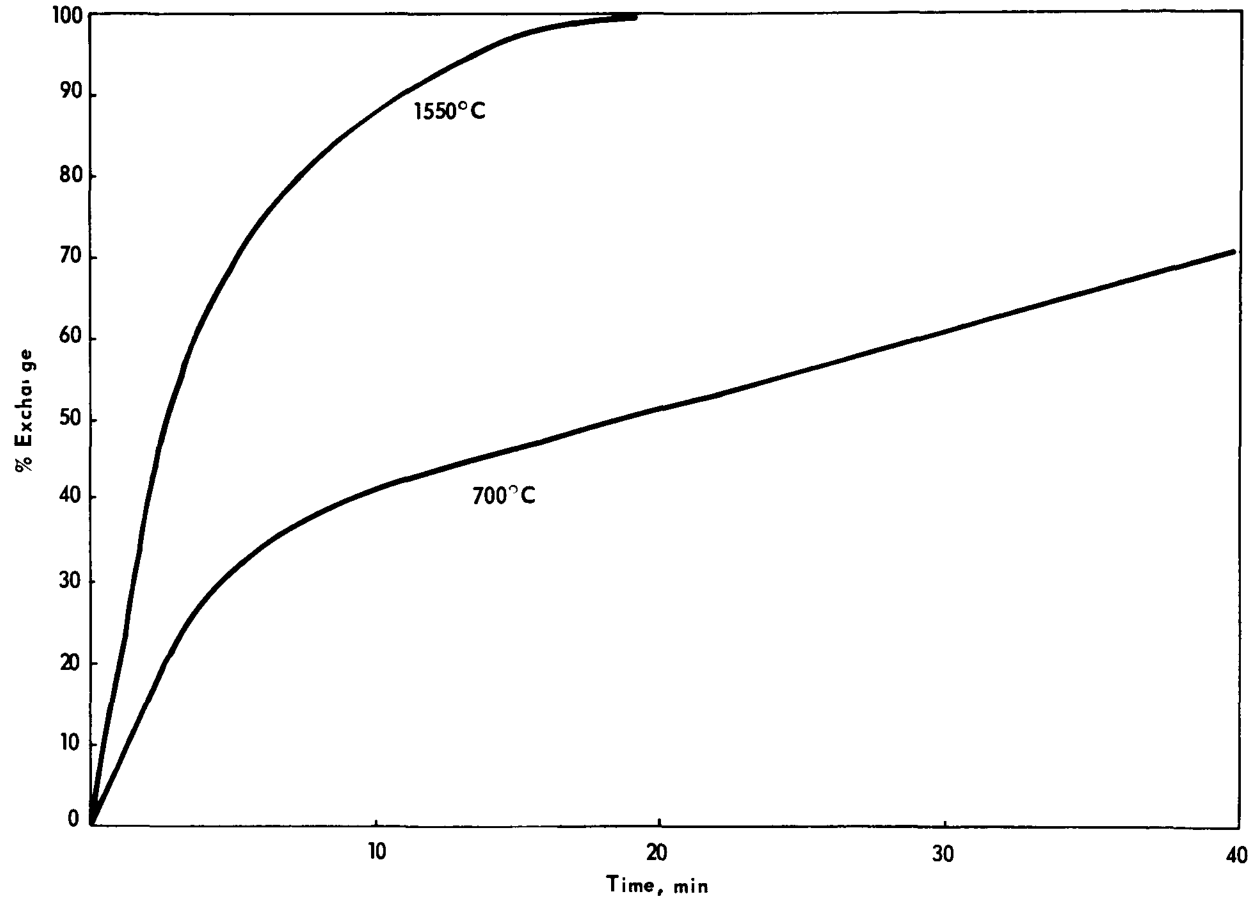

FIGURE 4 - Exchange of hydroxide PuO_2 at 700°C and 1550°C.

The average particle size of oxalate-prepared plutonium dioxide is of the order of several micrometers and this is therefore the limiting grain size. Since only one reaction was observed in the exchange of oxalate-prepared plutonium dioxide and since sintering does not lower the rate of exchange the surface reaction must occur to a depth of several micrometers. Hydroxide-prepared plutonium dioxide, on the other hand, has grain sizes of the order of 10-20 μm, and diffusion is required to obtain complete exchange. Apparently the diffusion of oxygen in plutonium dioxide is sufficiently rapid at 1550°C that exchange is readily achieved. Grain growth is apparently a slow process since the rate of exchange and hence diffusion at 1550°C does not change appreciably with additional sintering times as is shown in Table 4.

The present data lead to some important conclusions. The exchange of plutonium dioxide is very dependent upon the method of preparation. The proportion of self-diffusion and surface exchange reactions will determine the observed rate of exchange. Plutonium dioxide which has large grain sizes will exchange more slowly than that with smaller grain sizes. At 1550°C, however, self-diffusion is sufficiently rapid to permit any preparation of plutonium dioxide to undergo an oxygen exchange reaction to form $^{238}Pu^{16}O_2$.

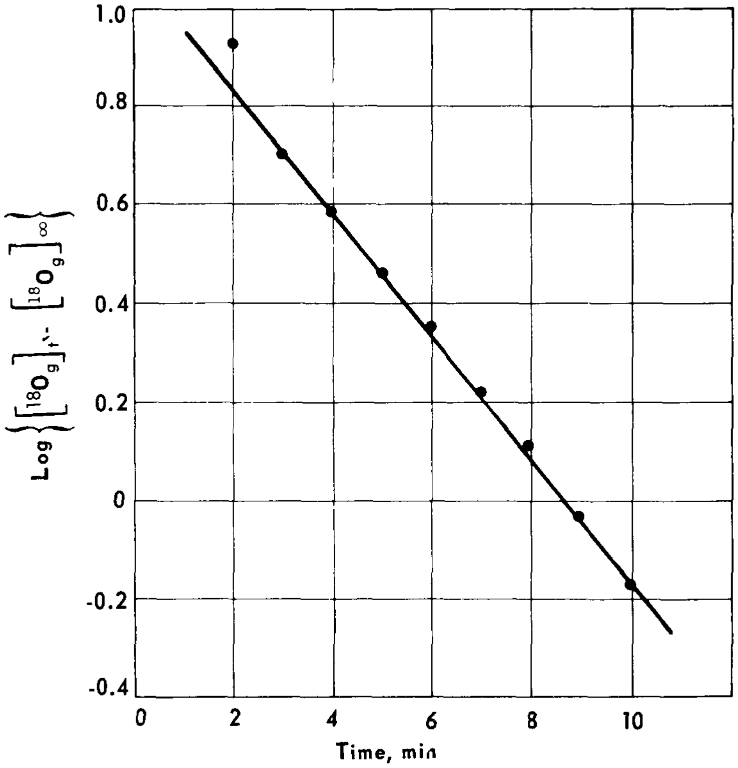

FIGURE 5 - Exchange of oxalate PuO_2 at 1000°C with respect to $^{18}O_2$(g).

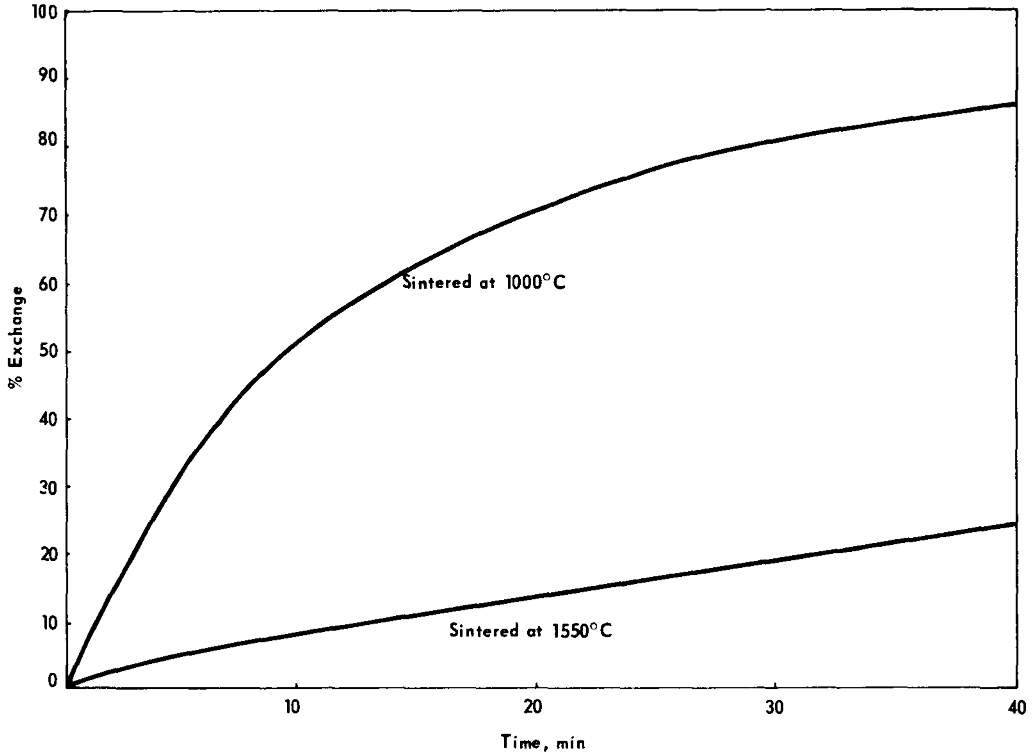

FIGURE 6 - Effect of sintering on exchange of hydroxide PuO_2 at 1000°C.

PART III

In Parts I and II of this report it has been shown that plutonium dioxide suitable as a fuel for radioactive heat sources will undergo oxygen exchange and that plutonium-238 dioxide with a low neutron flux can be prepared. On a production basis stepwise exchange of plutonium dioxide, such as was carried out in Part I, is not an economically feasible process. On a production basis it would be desirable to have a system whereby oxygen could be flowed over or through the plutonium dioxide.

The flow studies were carried out in a quartz apparatus which resembled a cold trap. The outer tube was 13 mm in diameter while the inner tube was 3 mm in diameter. Approximately 15 g of hydroxide-precipitated plutonium dioxide was exchanged at 700°C. The sample was heated to 700°C in air, then purged for one minute with oxygen-16 and the flow was set to the desired level. After the desired quantity of gas was flowed over the sample, the flow was reduced to less than 1 ml/min and the sample was sintered at 1200°C for one hour. The initial purge and the slow flow during sintering was small compared to the total amount of oxygen used for the exchange.

Figure 7 shows the results which were observed for the degree of exchange as a function of flow rate. The solid line indicates the points where 1.5 times the theoretical amount of oxygen was used. The dashed line suggests the shape of the curve at slower flow rates than were measured. Since it has been shown that by coupling exchange at 700°C and sintering at 1200-1400°C nearly complete exchange can be obtained, the point at infinitely slow flow rates represents complete exchange. Points A and B represent the degree of exchange at constant flow rates using 2.0 and 2.5 times the theoretical quantity of oxygen.

It is suggested that the important variable in this study is not the flow rate but rather the velocity of the oxygen-16 up the reaction tube and past the sample. Calculations using the bulk density of plutonium dioxide as 5.0 (this value has been observed in this laboratory) and the tube dimensions show that, in this system, the velocity of the gas past the sample in cm/min is numerically equal, or nearly so, to the flow rate in ml/min. No correction was made for the volume expansion of the gas as this is simply a constant factor regardless of the system being used. In comparing flow rates required for exchange at temperatures other than 700°C, the flow rate must be increased or decreased according to the relative gas expansions at the exchange temperature and 700°C.

It is unfortunate that these experiments were performed prior to obtaining the rate data presented in Part II. Undoubtedly, the fact that such a poor degree of exchange was obtained is due in part to the slow exchange reaction of hydroxide-precipitated plutonium dioxide at 700°C. Translating these data to the degree of exchange at temperatures other than 700°C requires that this fact also be taken into consideration.

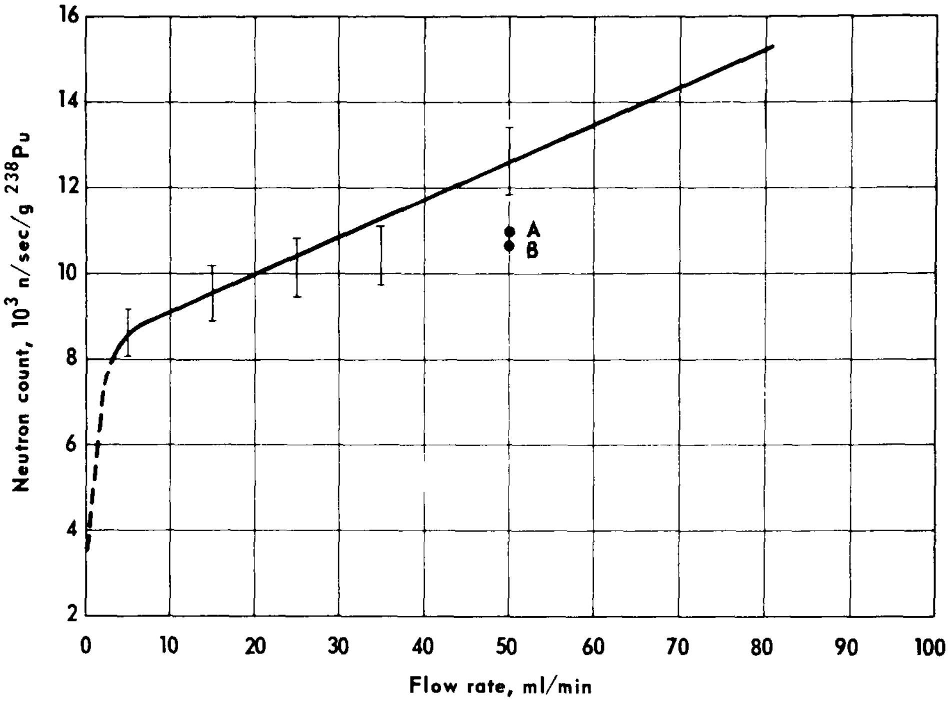

FIGURE 7 - The exchange of hydroxide-precipitated PuO_2 as a function of flow rate of oxygen-16.

Additional flow experiments were conducted on ¼-in. pellets prepared from 10 wt % ThO_2-PuO_2. These studies were carried out in a small bore furnace into which a 10 mm i.d. quartz tube could be placed. Exchange was carried out on four pellets placed end to end in the horizontal tube. The experimental procedure was the same as that for the hydroxide-precipitated plutonium dioxide with the exception that the pellets were sintered at 1300°C after exchange at 700°C.

The data presented in Figure 8 show the degree of exchange as a function of flow rate and velocity of gas past the sample. It is immediately apparent that the degree of exchange is considerably higher for the pellets than for the hydroxide-precipitated plutonium dioxide. Referring to the kinetic data for the exchange of oxalate plutonium dioxide one would predict greater exchange for these pellets than for the hydroxide material which is what was found. Also shown in Figure 8 is the exchange of pellets at 1200°C. One would expect very little increase in the degree of exchange at 1200°C since under the conditions used nearly complete exchange occurs at all temperatures.

The results presented in Part III show that exchange occurs under a flowing system. The effect of gas flow on degree of exchange is shown. It appears that for hydroxide-precipitated plutonium dioxide the temperature of the exchange is more important than the rate of flow of the enriched oxygen.

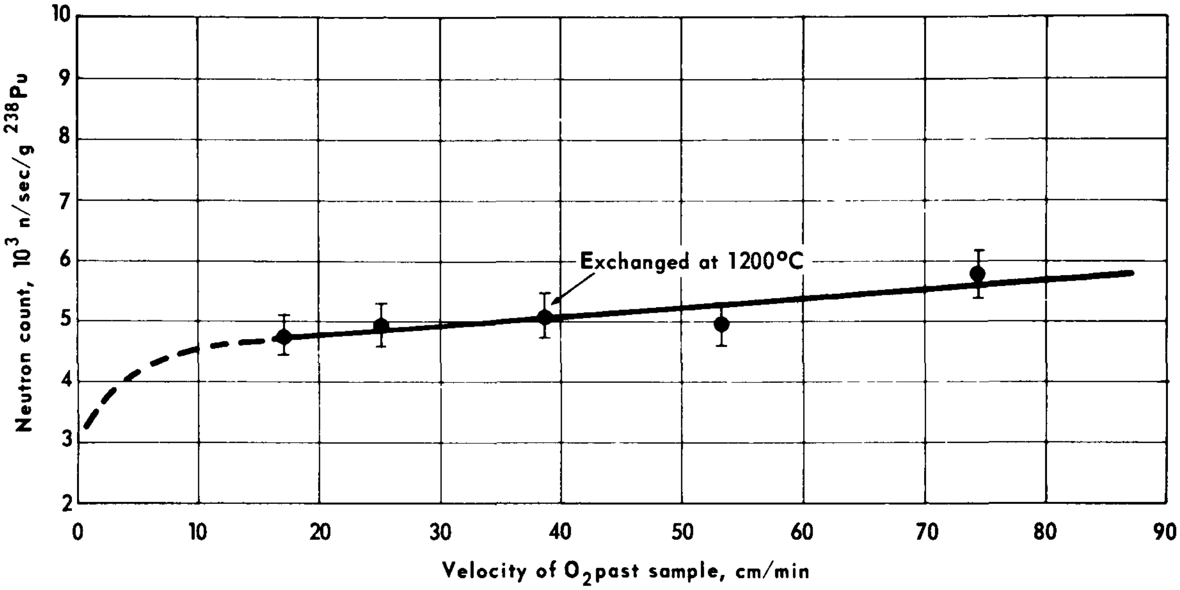

FIGURE 8 - The exchange of ThO_2-PuO_2 solid-solution pellets as a function of velocity of oxygen-16.

CONCLUSIONS

Normal as-received plutonium dioxide generally exhibits a neutron flux higher than that expected for material with a normal oxygen isotope distribution. This is generally attributed to light element impurities which may undergo an (α,n) reaction. The major impurity is believed to be the fluoride ion as HF is used in the dissolution of the plutonium oxide prior to precipitation. To obtain a heat source with a low neutron flux it is therefore necessary to remove these impurities in addition to preparing $^{238}Pu^{16}O_2$. The results of Part I indicate that outgassing or holding a sample under vacuum at 700°C is not sufficient to remove all these impurities. However, sintering at 1300°C is certainly sufficient to remove all the light element impurities and sintering at 1000°C may be sufficient; however, longer times may be required.

The removal of light element impurities is best accomplished during or after the exchange reaction since exchange is greatly affected by sintering, at least in the case of hydroxide plutonium dioxide or pellets of plutonium dioxide. It has been demonstrated that sintering may be accomplished during exchange or subsequent to exchange under an atmosphere of oxygen-16.

The best temperature for the exchange reaction is dependent upon the type of material being exchanged. Plutonium dioxide prepared from the oxalate undergoes fairly rapid and complete exchange at temperatures as low as 700°C. Increasing the temperature to 1550°C increases the exchange rate by a factor of three. Particles of plutonium dioxide with larger grain size such as hydroxide-prepared plutonium dioxide or sintered pellets will require temperatures approaching 1550°C to get complete exchange in a reasonable period of time. This is due to the fact that exchange of this material occurs by a diffusion process.

The results of sintering the sample after exchange is also dependent upon the material type. It was previously thought that by sintering the material count be "fixed" and reexchange with atmospheric oxygen would not occur. With oxalate plutonium dioxide sintering does not affect grain size as maximum grain size is determined by the particle size. The exchange reaction is therefore not diffusion controlled and sintering will not affect the exchange rate. Reexchange will probably be rather rapid at ambient temperatures, being completely reexchanged in a period of perhaps a week or two.

The reexchange of hydroxide plutonium dioxide is greatly retarded by sintering since there is considerable grain growth. Nevertheless, diffusion is apparently sufficiently rapid even at 200°C to cause complete reexchange in one month. Therefore, if a large mass of $^{238}Pu^{16}O_2$ is to be stored in air for considerable periods of time an oxygen-16 atmosphere will be required.

The best and most economical conditions for exchange will be with a flowing gas system. Good exchange occurs with slightly more than a theoretical amount of oxygen whereas stepwise exchange, although dependent upon experimental conditions, requires considerably more oxygen-16.

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